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Monitoring Strategies for Fluidized Bed Combustion Coal Plants

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MONITORING STRATEGIES FOR FLUIDIZED BED COMBUSTION COAL PLANTS

by

A.B. Garlauskas, C.E. Hina, T.T. Blair,
M.J. Kangas, and C.L. Cornett
Dalton·Dalton·Newport, Inc
3605 Warrensville Center Road
Shaker Heights, Ohio 44122

Contract No. 68-03-2755

EPA Project Officer
Richard Bateman
Advanced Monitoring Systems Division
Environmental Monitoring Systems Laboratory
P.O. Box 15027
Las Vegas, Nevada 89114

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16. ABSTRACT

Air and water monitoring strategies for commercial-size Fluidized Bed Combustion (FBC) coal plants are presented.

This is one of five reports developing air and water monitoring strategies for advanced coal combustion (FBC), coal conversion (coal gasification and liquifaction), and oil shale conversion commercial-scale plants. The objective of the five-part project is to assure that, when any of the coal or oil shale technologies become commercialized, appropriate and cost-effective monitoring requirements are in effect to protect the public health and the environment without delaying commercialization.

In this report, air quality monitoring strategies are presented for compliance audits, and for monitoring fugitive emissions. Water quality monitoring strategies are presented for leachates from fly ash and other solid wastes and from coal and sorbent material storage piles, and for pollutants generated by cooling towers, ponds, or canals.

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ABSTRACT

This report presents air and water monitoring strategies for commercial-size Fluidized Bed Combustion (FBC) coal plants. It is one of five reports developing air and water monitoring strategies for advanced coal combustion (FBC), coal conversion (coal gasification and liquefaction), and oil shale conversion commercial-scale plants. The overall objective of the five-part project is to assure that, when any of the coal or oil shale technologies become commercialized, appropriate and cost-effective monitoring requirements are in effect to protect the public health and the environment without delaying commercialization.

A detailed analysis of FBC processes was conducted to determine the quantities and nature of air and water effluents. Process data were obtained from former and existing small experimental and larger pilot plant FBC units. Data on the types and concentrations of pollutants were compiled and the effluent process streams identified. A pollutant selection and priority-ranking procedure was designed and used to determine which pollutants of the FBC processes needed monitoring.

Air and water quality monitoring approaches in the environment around an FBC plant were evaluated. Then air quality monitoring strategies were developed for compliance audits, for monitoring regulated pollutants from coal-fired plants, and for monitoring fugitive emissions. Water quality monitoring strategies were developed for leachates from fly ash and other solid wastes and from coal and sorbent material storage piles, and for pollutants generated by cooling towers, ponds, or canals.

Appropriate sampling procedures, analytical instrumentation, and general analysis methods were identified and selected. Monitoring data-interpretation approaches and reporting procedures were researched. A basic quality assurance program applicable to FBC and other fossil energy technologies was designed.

Conclusions and recommendations demonstrate that FBC plants present less undesirable environmental consequences and

are more efficient than conventional coal-fired plants. However, significant information gaps exist, preventing accurate extrapolation of experimental data to full commercial-scale FBC plants, and the current FBC environmental assessment program needs acceleration and better data dissemination. A number of specific recommendations were developed.

This report covers the period October 1, 1978, to September 30, 1979.

CONTENTS

Abstract iii
Figures x
Tables xii

SECTION 1 - INTRODUCTION. 1

- Purpose and Scope. 1
- Monitoring Systems 2
- Monitoring System Design Considerations. 6
- Report Organization. 10

SECTION 2 - FLUIDIZED BED COMBUSTION OF COAL: PROCESS, ENVIRONMENTAL POLLUTANTS, AND POLLUTION CONTROL. 11

- Background 11
- Process Description. 14
  - Basic Principles 14
  - Atmospheric Fluidized Bed Combustion of Coal . 19
  - Pressurized Fluidized Bed Combustion of Coal . 22
- Environmental Pollutants from FBC of Coal. 24
  - Methods of Determining Pollutants. 24
  - Sources and Major Types of Pollutants. 27
  - Environmental Pollutants 28
  - Flue Gases and Particulates. 34
  - Solid Wastes and Leachates 47
  - Sorbent Leachate 48
  - Boiler Blowdown. 48
  - Cooling System Effluents 48
  - Sorbent Regeneration 51
  - Biological Examination 55
- Pollution Control. 55
  - Background 55
  - Pollution Control of Flue Gases. 60
    - General Pollution Control Applications . 60
    - Carbon Utilization 62
    - Nitrogen Oxide Reduction 63
    - Sulfur Dioxide Reduction 68
    - Particulate Matter 73
- Outlook. 73

EPA Form 2350-4 (4-80)
(PREVIOUSLY C/H. EPA FORM 327)
TYPING GUIDE SHEET

SECTION 3 - SELECTION OF POLLUTANTS FOR MONITORING 81

- Introduction 81
- Assumptions. 85
- Categorization 87
  - Overview 87
  - Species Identification 87
  - Media Determination. 88
  - Identification of Standards and Criteria for Specific Chemical Components of the Effluent Streams 88
  - Identification of Extremely Hazardous or Toxic Substances. 89
  - Summary of the Categorization Process. 91
- Priority Ranking 91
  - Overview 91
  - Identification of the Potential for Receptor Damage from Unregulated Pollutants 92
  - Identification of Emission Rates and Ambient Level Concentrations 101
  - Methods of Combining Effects and Concentration Values to Estimate Hazard Potential. 104
- Development of a Decision Rule to Select Pollutants For Monitoring Based on Their Potential for Environmental Hazard 108
- Preparation of the Preliminary List of Pollutants to be Monitored. .109
- Final Selection of Pollutants Based on Technical and Cost Considerations. 109
  - Technical Quality of Available Analytical Methods. 110
  - Cost Considerations. 113
- Conclusions. 118

SECTION 4 - AIR QUALITY MONITORING STRATEGIES. 119

- Introduction 119
- Air Quality Impact Generators. 120
- Conditions Where Ambient Monitoring Is Indicated . .120
- Regulations. 124
  - New Source Performance Standards 124
  - Prevention of Significant Deterioration. . . .126
  - Monitoring Requirements. 129
- Selection of Pollutants to be Monitored. 131
  - Introduction 131
  - Categorization and Prioritization. 132
    - Category I Pollutants. 132
    - Category II Pollutants 133

Estimation of Expected Ambient Concentration of Problem Pollutants. 133
Preliminary List of Pollutants for Monitoring.133
Monitoring Network Design and Dispersion Models. . .133
  Background 133
  Air Monitoring Network Design. 134
Monitoring Strategies for FBC Installations. 137
  Background 137
  Compliance Audit Monitoring. 137
    Methods of Measurement 139
    Ratio of Components Techniques 139
      Upwind/Downwind Sampling 139
      Differential Plume Impact Monitoring 139
    Remote Sensing 142
    Dispersive Correlation/Spectroscopy . . 145
      Non-Dispersive Gas Filter Correlation Spectrometer (GFC) .148
      Ultraviolet Television Sensor. . .148
      Emission Rates for Other Materials. 150
  Level 1 and Level 2 Assessment Monitoring. . .151
  Fugitive Emission Monitoring 161
    Heat of Hydration and Alkalinity 162
    Portable Wind Tunnel Monitoring. 164
    Sulfates, Sulfites, and Organic Adduct Analysis 165
    Long-Range Plume Transformation Studies. 168
    Short-Range Plume Transformation Studies. 169
    Balloon-Borne Sampling System. 169
  Opacity Measurements 171
    Opacity Mass Concentration Relationship 172
    Special Considerations for Fluidized Bed Combustion Units 176
    Applications of Opacity/Mass Concentration Relationships. 176
    In-Stack Opacity Measurement 178
    Remote Measurement of Plume Opacity. . .179
      Trained Observers. 179
      The Method of Contrasting Targets. 180
        Laser Radar. 181
        Sun Photometer 181
Data Reporting 181

SECTION 5 - WATER QUALITY MONITORING STRATEGIES. 183

- Introduction 183
- Impact Generators. 184
- Conditions Where Water Quality Monitoring Is Indicated. 185
- Selection of Pollutants To Be Monitored. 190
- Groundwater Monitoring 197
- Surface Water Monitoring 197
- Physical Sinks 198
- Biological Sinks 199
- Considerations Specific to Surface Water Monitoring.200
  - Definition of the Watershed and Hydrological System 200
  - Transport of Pollutants in Surface Aquatic Systems. 201
- Considerations Specific to Groundwater Monitoring. .202
  - Evaluation of Ability of Pollutants to Percolate From Land Surface to the Zone of Saturation 204
  - Evaluation of Attenuation of Pollutants in the Vadose Zone 205
  - Evaluation of Attenuation of Pollutants in the Zone of Saturation. 206
- Sampling 207
  - General Considerations 207
    - Number and Location of Sampling Points .207
    - Frequency of Sampling. 208
    - Sample Volumes 209
    - Sample Preservation. 209
  - Sampling Equipment 210
    - Manual Samplers. 210
- Analytical Methods 214
  - Approved and Standard Methods. 214
  - Trace Organics 221
  - Biological Methods 221
  - Level 1/Level 2 Analysis 223
  - Data Recording 225
- Data Handling. 230
- Data Analysis. 230
  - Regression Analysis. 230
  - Time Trend Analysis. 231
  - Factor and Principal Component Analysis. . . .231
  - Water Quality Indices. 232
  - Water Quality Models 233

SECTION 6 CONCLUSIONS AND RECOMMENDATIONS. 235

- Conclusions. .235
- Recommendations. 235

EPA Form 2350-4 (4-80)
(PREVIOUSLY EIN. EPA FORM 287)

TYPING GUIDE SHEET

REFERENCES 239

APPENDICES

A. Guidelines for Developing a Quality Assurance Program for Ambient Monitoring Associated With Energy Technologies. 259

B. List of Laws, Regulations, and Executive Orders Pertaining to Environment and Safety and Health Requirements. 297

EPA Form 2350-4 (4-80)
[PREVIOUSLY ZIN EPA FORM 257]

TYPING GUIDE SHEET

FIGURES

Number		Page
1	Multimedia Sampling Approach Overview	7
2	Selected FBC System Options	18
3	Schematic Diagram of Atmospheric Pressure FBC Boiler	20
4	Schematic Diagram of Pressurized FBC Boiler with Sorbent Regeneration	23
5	Generic Schematic of FBC Unit Operations With Numbered Process Flows Producing Waste Streams	29
6	Schematic Diagram of Emission Sources Within Atmospheric-Pressure FBC Plant	30
7	Scheme of FBC (Materials Flow)	49
8	Air Pollutant Particle Sizes	58
9	Emission Control Equipment Chart	59
10	Effect of Oxygen Concentration on Hydrocarbon Emission	64
11	Nitrogen Oxides Emissions (expressed as NO_2) From Atmospheric Fluidized Bed Combustion Units	65
12	Nitric Oxide Reduction With -325 Mesh (<44 μm) Tymochtee Dolomite	66
13	Effect of Gas Velocity on Nitric Oxide Reduction in Flue Gas	67
14	Composite Plot of Data for NO_x Emissions from Fluidized Combustion of Coal	67

Number **Page**

15 Sulfur Removal Performance for Typical Sorbents (Projected using Westinghouse Kinetic Model) 69

16 FBC Power Plant Energy Conversion Efficiency 70

17 Schematic Flow Diagram of the Precalcination Process. 72

18 Total Solids from Combustor (AFBC). 74

19 CFCC Particulate Emissions 75

20 Design of an Ambient Monitoring Program. 83

21 Procedure for Selecting Pollutants for a Source-Oriented Ambient Monitoring Plan. 86

22 Methodology for Deriving MATEs from Empirical Data 95

23 Methods Selection-Technical Aspects. 111

24 Methods Selection - Cost Aspects 114

25 Differential Plume Impact Data 141

26 Basic Level 1 Sampling and Analytical Scheme for Solids, Slurries, and Liquids 153

27 SASS Analysis Requirements 154

28 Flue Gas Sampling Flow Diagram 155

29 Source Assessment Sampling Train Schematic . . .156

30 Fugitive Air Sampling Train Components 157

31 Integrated Gas-Sampling Train. 159

32 Schematic of Second Generation Sampling Package. 170

33 K as a Function of Log Normal Size Distribution Parameters. 173

34 Data Flow in a Source-Oriented Ambient Monitoring Program 227

TABLES

Number		Page
1	Arithmetic Mean of Proximate and Ultimate Analysis and Elemental Composition for Coals from Various Basins	12
2	Types of Potentially Harmful Pollutants Associated With FBC Technology	13
3	Alternative Sorbent Selection	25
4	Stream Designations for Generic Units	28
5	Radioactivity Measurements	33
6	Reported Ranges of Some Minor Stack Flue Gas Constituents	35
7	Volatile Element Analysis in Flue Gas	37
8	Projected Flue Gas Emission of Trace Elements as a Percentage of the Element Entering the System	37
9	Potential Enrichment of Elements in the Fine Particulate Catch	38
10	Inorganic Elements and Compounds Identified in Flue Gas Particulates	42
11	Polycyclic Organic Material Analysis	43
12	Inorganic Analysis of Particulate Emissions in Flue Gas	45
13	Trace Metals in Bed Reject Material	46
14	Pollutants From Leaching of Coal Piles	50
15	Chemical Agents Associated With Boiler Treatment	50

Number **Page**

16 Chemicals Used in Recirculative Cooling Water Systems. 52

17 Cooling Tower Corrosion and Scale Inhibitor Systems. 52

18 Representative Concentrations of Elements in Leachate of FBC Spent Bed Material 54

19 Leachates from Flue Gas Particulates Collected from FBC Processes. 54

20 POM Compounds in Leachates from AFBC and PFBC Combustion of Coal Solid Wastes. 56

21 Anion Analysis of Leachate of FBC Solid Wastes 56

22 Major Contaminants in the Flue Gas of Fluidized Bed Combustion and Applicable Pollution Control Equipment. 61

23 Distribution of Combustible Losses 62

24 Predicted Ca/S Requirements for the Atmospheric Fluidized Bed Combustor. 71

25 Properties of the Particles Suspended in the Flue Gas 74

26 Factors Influencing the Commercialization of Fluidized Bed Combustion of Coal 79

27 Criteria Used to Identify Extremely Toxic Substances 90

28 Emission Level Goals Foundations 94

29 Basic Data and Derivations for Ambient Level Goals. 96

30 Approaches to Estimating Ambient Level Goals (ALG) Which Function as Minimum Potential Hazard Levels in the Ambient Environment . . . 102

31 Approaches to Estimating Ambient Environmental Concentrations Expected to Impact Human and Environmental Receptors. 103

32 Sources of Atmospheric Emissions 121

Number Page

33 Federal Standards of Performance for New Stationary Sources of Air Pollution. 125

34 Allowable Increases in Ambient Pollution Levels Under PSD Regulations 127

35 Ambient Air Quality Standards. 128

36 Assumed Natural Background Concentrations. . . 130

37 Comparison of In-Stack and COSPEC II SO_2 Concentration Measurements 149

38 Summary of Average Values of Remote GFC and Extractive Data. 149

39 Comparison of SO_2 Concentration and Effluent Velocity Measurements By Video and In-Stack Techniques. 150

40 Basic Level 1 Analyses 152

41 Applicable Ambient Water Quality Standards . . 189

42 Summary of Pollutants Segregated Among Categories 194

43 Selected EPA Effluent Standards for Steam Electric Power Generating Plants 196

44 Volume of Sample Required for Determination of the Various Constituents of Industrial Water. 211

45 Summary of Preservation Methods for Water Samples. 212

46 State-of-the-Art Water Quality Methods: Non-Metals 216

47 State-of-the-Art Water Quality Methods: Metals 218

48 Atomic Absorption Concentration Ranges 219

49 Criteria for Selection of Analytical Methods. 220

Number		Page
50	Organics for Which Discrete Analytical Methods Have Been Developed	222
51	NAWDEX Participating Data Systems.	228

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SECTION 1

INTRODUCTION

PURPOSE AND SCOPE

This report presents strategies for source-oriented ambient air and water pollutant monitoring of commercial-scale Fluidized Bed Combustion (FBC) coal plants. This is the first of five monitoring strategy reports to be completed under the overall project, Air and Water Monitoring Guidelines for Advanced Coal Conversion and Combustion Plants. Each report develops monitoring strategies for one of the following:

- Fluidized Bed Combustion of Coal
- Low/Medium BTU Gasification of Coal (surface and in situ)
- Oil Shale Conversion
- Coal Liquefaction
- High BTU Gasification of Coal

The strategy report for each technology focuses analytically on environmental requirements as these technologies move to commercialization. Each technology is dealt with generically wherever possible and appropriate. The reports are not technical monitoring manuals; they are monitoring policy guidance reports, to help the U.S. Environmental Protection Agency (EPA) evaluate monitoring requirements for emerging energy technologies.

The basis for the project is to ensure that when one of the new fossil technologies (four coal, one shale) is ready to move to commercial status, it will not be delayed by inadequate, inappropriate or unavailable environmental monitoring requirements. The guidance reports will help to determine the most likely candidate technologies and to develop the strategies for environmental monitoring before these technologies are ready for commercialization, to assure that they will be moved rapidly ahead on a sound environmental basis.

The monitoring strategies are based on "ambient" conditions, rather than only on the products at the end of the

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"stack." Thus, they identify pollutants, their paths upon leaving the stack or pipe, and their transformation before they reach the ground, people, plants, or animals.

These monitoring strategies/approaches will provide a critical link between traditional "stack pipe" monitoring and the study of their effects on plants, people, and animals, and will make the final required monitoring programs both more cost-effective and more closely associated with actual effects.

If the development of environmental monitoring strategies is delayed, the implementation of the associated technologies may also be delayed. It is important to maintain and expand this effort to:

- Ensure that EPA regulations are adequate, appropriate, realistic, and cost-effective.
- Ensure cost-effective monitoring programs.
- Ensure that the development of energy technologies is not delayed because of lack of regulatory requirements.
- Minimize the cost of development, both for technologies and for environmental control.

MONITORING SYSTEMS

Environmental monitoring, a systematic and scientific approach to assuring a congruous interface between natural and man-made systems, is an essential component of environmental management. It serves to minimize the impact of man's activities through the resolution of the conflicts that arise from human activities on the natural environment.

The EPA has the major responsibility to assure that the country's environment is properly managed. With proper management tools, the Agency can gather data to develop and maintain an adequate environmental monitoring capability. A systems approach to data-gathering links private and governmental monitoring systems, to provide data that complies with environmental monitoring regulations and degree-of-accuracy requirements. EPA monitoring systems, augmented by other governmental and private systems, can provide a sound basis for decision-making. Critical aspects of a problem can be adequately analyzed and findings incorporated early in the design and control strategy phases. This is especially important with emerging energy technologies that have unknown or partially known effects on the environment.

The three basic categories of environmental monitoring are source monitoring, ambient monitoring, and effects monitoring. Each has its strengths and weaknesses. When properly linked in a systems approach, each category fills data gaps, assures the correlation and continuity of data from source to effect, and reinforces the data base on any scale of analysis--national, regional, global, or local. The measurement systems of each monitoring category can be remarkably different but, with clearly defined linkages and data correlation techniques, they can produce a comprehensive data base that will demonstrate environmental acceptability or non-acceptability of a specific energy conversion plant or the entire energy technology. Definitions of each category of monitoring are given in the following paragraphs.

Source monitoring refers to measurements taken at the point or points at which pollutants escape or are discharged into the environment. Source monitoring seeks to determine what residuals enter or will enter the environment, from what sources, and in what amounts. It serves in enforcing compliance with emission standards; forecasting those activities of production, storage, transportation, use and disposal that may cause pollution; and taking inventory of emissions from production processes. Sources include point sources (industrial stacks, discharge pipes, and other stationary sources), area or non-point sources (groupings of small sources spread over regions [cities, farmlands, forests]), and mobile sources (automobiles, aircraft, trucks, buses, railroads, pipelines, ships). The latter include spills of toxic and other hazardous materials during transport (National Research Council, 1977).

Ambient ("surrounding on all sides") monitoring refers to the measurement of concentrations of pollutants in the air, water, soil and biota; it is designed to determine what concentrations of residuals are present in air, water, soil, food and animal tissues (National Research Council, 1977). A more restricted definition of ambient monitoring can be developed from the EPA definition of ambient air as "that portion of the atmosphere, external to buildings, to which the general public has access" (U.S. EPA, 1979c); in which case, ambient monitoring can be defined as monitoring air and water to which the general public has access.

Effects monitoring is designed to determine the consequences of current and potential pollutants on humans, animals, plants and materials, and to evaluate their economic, social, and aesthetic costs (National Research Council, 1977). Some examples of effects monitoring are: epidemiological studies of disease occurrence in human populations

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where the causal factors are related to environmental pollution; disease detection programs based on continuing surveillance of particular groups of people who are or have been exposed to chemicals known to be animal carcinogens but not yet identified as human carcinogens; monitoring of occupational health statistics; and monitoring of animals and plants to determine how chronic exposure to low-level pollutants affects them. Monitoring of ecological systems includes productivity, diversity, fecundity, bioaccumulation, and other important aspects of biological species on plots in natural ecosystems (such as a watershed for terrestrial life or river for aquatic life); and productivity of major agricultural crops, forage, and forests on selected field plots (National Research Council, 1977).

The application of source, ambient, and effects monitoring to special purposes and in combination with each other has created variants of monitoring categories with specialized meaning. One such sub-category is source-oriented ambient monitoring, as used in this report. This specialized form of ambient monitoring is designed to monitor pollutants, hazardous wastes, and toxic substances (pollutants) in an area where they can be in some way attributed to a specific source. Source-oriented ambient monitoring also focuses on the derivatives of pollutants, hazardous materials, and toxic substances which are transformed upon release into the ambient environment including air, water, land, and living tissue.

The goals and objectives of source-oriented ambient monitoring are to:

- Separate out the materials in the environment directly attributable to a source from the background concentrations.
- Monitor those substances and materials that cannot be monitored at the point of discharge (e.g., fugitive emissions).
- Monitor the substances that are transformed upon release from the source into the ambient environment (including in living tissues).
- Serve as a link between source monitoring and effects monitoring by providing the necessary information of what path a substance takes in the ambient environment upon release from a source to its final site of action. In this way, source-oriented ambient monitoring helps establish cause/effect relationships.

Source-oriented ambient monitoring, then, traces energy source effluents from the source to the ambient environment. This approach, which is of critical importance in establishing clear pollutant pathways and impacts, relies heavily on the availability of sound ambient environmental quality baseline data. Although at least eight different federal agencies monitor environmental quality systematically throughout the nation in different regions (Morgan, 1978), the type of information generated by these agencies is primarily geared toward conventional pollutants. The certainty of development of additional coal and oil shale resources and their processing for energy generation has created the need for monitoring non-conventional pollutants that will be generated from these new energy sources. Although FBC of coal does not appear to be a hazardous or toxic-waste-producing technology, based on current and anticipated regulations, other fossil fuel combustion and conversion technologies such as coal gasification or liquefaction, or oil shale extraction may generate significant toxic or hazardous pollutants.

Based on the above considerations, a monitoring system must 1) establish a sound baseline of toxic pollutants in the ambient environment before energy developmend, and 2) detect changes in any of the pollutants or introduction of new toxics following energy source development. The type of monitoring, the pollutants to be monitored, and the methods to be used should be determined before new technologies are commercialized, to allow development to proceed within a sound environmental framework.

In this context, monitoring should be "anticipatory," focusing on on-going surveillance of air, surface water, and groundwater for potential changes in concentrations of specified toxic substances which may be induced by the development of energy resources and/or technologies in the region of interest. Its scope is defined by:

- Types of energy resources likely to be developed in the region
- Toxic pollutants expected to be associated with them
- Nature of the technology and its associated pollution controls and waste disposal methods
- Extent of the air regions affected
- Types of water uses likely to be impacted by these pollutants in the region in question

- Most probable loci of these impacts.

The goals of anticipatory monitoring are to:

- Establish baseline concentrations of toxic substances in the air and water regions of interest so that future changes can be detected before they adversely affect water uses
- Focus monitoring efforts on the air and water regions most likely to be impacted by particular types of energy resource development
- Focus monitoring efforts on the pollutants most likely to adversely affect air quality and water uses
- Determine whether there are reliable correlations among various pollutants associated with a given energy resource/technology and/or geographic area, to identify the significant "indicator species" that should be routinely monitored.

MONITORING SYSTEM DESIGN CONSIDERATIONS

Development of a source-oriented ambient monitoring program requires, as a first step, delineation of specific objectives. Also, the program should be visualized in the proper perspective; as Figure 1 illustrates, it is multimedia. Objectives of a source-oriented monitoring program should include:

- Accurate and complete characterization of ambient air and surface and groundwater conditions in the vicinity of the sources and for areas expected to be impacted by discharges.
- Monitoring air, surface water, groundwater, and associated media for contamination resulting from operation of FBC units.
- Documentation of existing and continuing ecological conditions.
- Protection of the public against unexpected plant discharges.
- Maintenance of records for the protection of the plant operator against any liability claims.

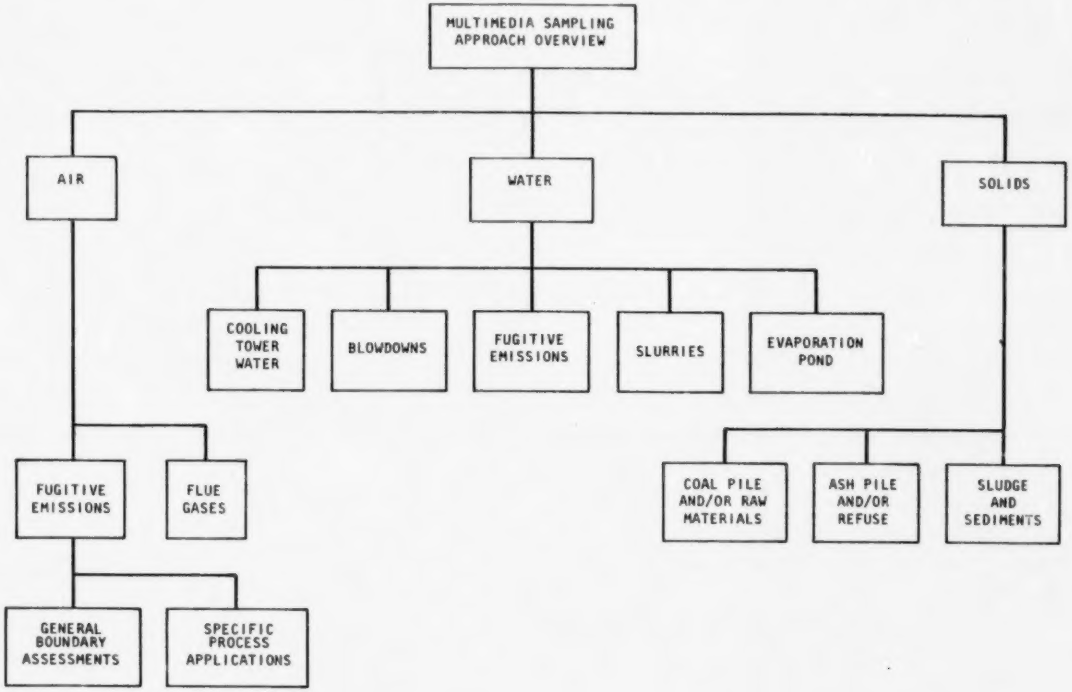
MULTIMEDIA SAMPLING APPROACH OVERVIEW
AIR
WATER
SOLIDS
COOLING TOWER WATER
BLOWDOWNS
FUGITIVE EMISSIONS
SLURRIES
EVAPORATION POND
FUGITIVE EMISSIONS
FLUE GASES
COAL PILE AND/OR RAW MATERIALS
ASH PILE AND/OR REFUSE
SLUDGE AND SEDIMENTS
GENERAL BOUNDARY ASSESSMENTS
SPECIFIC PROCESS APPLICATIONS

Figure 1. Multimedia sampling approach overview.

- Accumulation of data to assist in the improvement of pollutant dispersion models and estimation of impacts for future coal-fired FBC units.

- Provision of data for use in describing potential new source performance standards for FBC units.

The activities involved in monitoring air and water quality will be similar, whether the program is designed to determine compliance to ambient environmental quality standards, to identify sources of pollutants, or to determine impacts of a specific source. The general operational activities of a source-oriented ambient monitoring program are:

- Network Design
- Sample Collection
- Laboratory Analysis
- Data Handling
- Data Analysis
- Information Utilization

Each major activity contains a subset of specific elements which must be considered and described in detail prior to initiation of actual monitoring operations. The following monitoring system activity list has been adapted from Ward (1979).

- Network Design
    - Statement of objectives
    - Parameter selection
    - Sample station location (macro-location)
    - Sampling frequency

- Sample Collection
    - Sampling point (micro-location)
    - Field measurements
    - Sampling technique
    - Sample preservation
    - Sample transportation
    - Quality assurance

- Laboratory Analysis
    - Selection of analytical methods
    - Operational procedures
    - Quality assurance
    - Data recording

- Data Handling
  - Data reception from laboratory or outside sources
  - Screening and verification
  - Storage and retrieval
  - Data reporting
  - Dissemination

- Data Analysis
  - Basic summary statistics
  - Regression analysis
  - Air and water quality indices
  - Interpretation of quality assurance data
  - Time series analyses
  - Air and water quality models

- Information Utilization
  - Reporting formats
  - Information needs
  - Evaluation of overall program
  - Data utilization evaluation

Applications of source-oriented ambient monitoring are for:

- Detecting pollutant transformations occurring during transport to their site of action

- Establishing the links between source of pollution and effects (cause/effect)

- Calibrating emission models

- Auditing accuracy of emission inventory data obtained by conventional techniques (sources tend to be more careful of their operations during conventional emission tests than they might otherwise be)

- Obtaining entry warrants for conventional monitoring, by showing probable cause to suspect violation of standards

- Determining underground water flow patterns and dilution. Also can be useful in complex terrains, where modeling often breaks down

- Investigating complaints

- Monitoring groundwater around hazardous waste disposal areas, under proposed Resource Conservation and Recovery Act (RCRA) regulations (12-18-78), would be required and air monitoring might be

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TYPING GUIDE SHEET

required as a permit condition on a case-by-case basis. This contract could help to define what to monitor:

- Measuring emission rates from flares and fugitive sources that cannot be measured by more conventional techniques
- Researching the health and ecological effects of emerging technologies
- Providing for an alarm system for hazardous fugitive emissions (e.g., polynuclear aromatics [PNAs] from coal gasification)
- Supporting enforcement actions by providing documentation of the significance of the impact of a source, for legal action if necessary; helping to document the seriousness of impact in a way that is less theoretical than modeling--may help confirm the results of modeling
- Increasing the store of knowledge regarding pollutant transport, diffusion, and accumulation on a small geographic scale.

REPORT ORGANIZATION

Section 2 of this report reviews the FBC process, defines the effluents, identifies the sources of pollutants and their control, and reviews the commercialization outlook for this technology. Section 3 presents a procedure for selecting pollutants to be included in a monitoring program of FBC commercial-scale plants. Section 4 discusses air quality monitoring methods and approaches for FBC facilities, and Section 5 discusses water quality monitoring systems and methods applicable to FBC plants. Sections 4 and 5 also discuss quality control and quality assurance and reporting procedures. Quality assurance is treated in detail in Appendix A. Section 6 presents major conclusions and recommendations.

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SECTION 2

FLUIDIZED BED COMBUSTION OF COAL: PROCESS, ENVIRONMENTAL POLLUTANTS, AND POLLUTION CONTROL

BACKGROUND

Coal, which represents about 85 percent of the United States fossil fuel resources, will almost certainly be used to fulfill a major portion of the country's energy needs in the very near future. Coal can be readily extracted and is available in accessible geographic locations, and its utilization can fill the gap created by diminishing oil supplies. Increased use of coal will create different stresses on the economy, environment, and technology. Coal use currently constitutes about 18 percent of the U.S. energy consumption. How soon coal will fill the energy gaps and increased requirements will be a function of conservation, environmental regulations, tax laws, economics and developing technologies.

Coal is a complex, heterogeneous material containing organic and mineral matter. The organic matter is composed primarily of carbon and small amounts of hydrogen, nitrogen, oxygen, and sulfur. The mineral matter consists chiefly of clay minerals, mineral forms of sulfur (mostly pyrite), calcite, and smaller amounts of other minerals. Its composition is a fossil record of the geochemistry occurring at the time the original material from which the coal formed was deposited. Geochemical and coalification processes effected changes in heat, water, mineralogy, and, importantly, in sulfur content, with changes in the concentration and abundance of minor and major trace elements. Table 1 summarizes the elements and concentration ranges for coals from four basins. The inorganic constituents in coal are minerals derived from the surrounding rocks and incorporated into the coal seam.

The burning of coal releases most of the constituents into the environment in some form, creating public health and environmental problems. Many of the elements and compounds are injurious to any form of life even in small quantities. Some elements such as rubidium are toxic only in large quantities and concentrations. Elements that are extremely toxic even in small quantities are arsenic, beryllium, cadmium, lead, and mercury. To understand and deal with toxic elements

TABLE 1. ARITHMETIC MEAN OF PROXIMATE AND ULTIMATE ANALYSIS AND ELEMENTAL COMPOSITION FOR COALS FROM VARIOUS BASINS

Constituent		Appalachian coal[a]	Pennsylvania anthracite[a]	Illinois Basin coal[b]	North Dakota lignite[a]
Moisture	%	2.8	1.4	10.02	29.7
Volatile matter	%	31.6	6.5	39.80	29.6
Fixed carbon	%	54.6	79.5	48.98	32.1
Ash	%	11.0	12.6	11.28	8.6
Hydrogen	%	4.9	2.4	4.98	6.1
Carbon	%	72.6	80.1	70.69	43.1
Nitrogen	%	1.3	0.8	1.35	0.7
Oxygen	%	7.8	3.2	8.19	40.0
Sulfur	%	2.3	0.8	3.51	1.5
Heating value	MJ/kg	30	29.7	29.6	16.7
Elements	g/kg				
Aluminum		16.	20.	12.2	3.7
Antimony		0.0012	0.0009	0.0135	0.0003
Arsenic		0.027	0.006	0.1491	0.0067
Barium		0.11	0.1		0.4
Beryllium		0.002	0.002	0.0172	0.0002
Bismuth		0.0001	<0.0001		
Boron		0.030	0.01	1.138	0.12
Bromine		0.011	0.001	0.1527	
Cadmium		0.0007	0.0003	0.0289	0.0001
Calcium		1.2	0.7	7.4	12.
Chlorine		0.72	1.5	1.5	0.17
Chromium		0.020	0.02	0.1410	0.002
Cobalt		0.007	0.007	0.0915	0.001
Copper		0.024	0.0027	0.1409	0.0052
Fluorine		0.080	0.061	0.5930	0.026
Gallium		0.007	0.007	0.0304	0.0014
Iron		19.	4.4	20.6	13.
Lead		0.0153	0.01	0.3983	0.0034
Lithium		0.0276	0.033		0.0021
Magnesium		0.68	0.6	0.5	3.43
Manganese		0.62	0.02	0.5316	0.048
Mercury		0.00024	0.0002	0.0021	
Molybdenum		0.003	0.002	0.0796	
Nickel		0.015	0.02	0.2235	0.002
Niobium		0.005	0.003		0.0022
Phosphorus		0.09	0.075	0.6277	0.32
Potassium		2.3	2.4	1.6	0.2
Scandium		0.005	0.005		0.0012
Selenium		0.0047	0.004	0.0199	0.0008
Silicon		27.	27.	23.9	8.5
Silver		0.00003	0.003		0.002
Sodium		0.32	0.5	0.5	3.57
Strontium		0.1	0.1		0.34
Telluvium		0.00034	<0.0001		
Thallium		0.0001	0.05		
Thorium		0.0048	0.003		0.0035
Tin		0.0024	0.001	0.0456	0.0004
Titanium		0.9	1.5	0.6	0.33
Uranium		0.0014	0.002		0.0007
Vanadium		0.02	0.02	0.3313	0.004
Ytterbium		0.001	0.001		0.0002
Yttrium		0.01	0.01		0.003
Zinc		0.02	0.016	3.1304	0.0033
Zirconium		0.05	0.05	0.721	0.01

[a] DeAngelis and Reznik, 1979.

[b] Ruch et al., 1974.

is essential in developing viable coal utilization technologies. Compounding the problem of toxic elements are the complex organic and less complex inorganic compounds that are formed during combustion of coal. Many of them are toxic or otherwise injurious to living forms. Table 2 shows some of the major toxic elements and compounds released by combustion of coal.

TABLE 2. TYPES OF POTENTIALLY HARMFUL POLLUTANTS ASSOCIATED WITH FBC TECHNOLOGY
(Cornaby et al., 1977)

General category	Examples
Emissions of Single Chemicals	Cadmium, Chromium (Heavy Metals) Carbon Monoxide (Toxic Gases) Radionuclides Other
Emissions of Aggregated Chemicals	Total Hydrocarbons Oxidants Sulfates Radionuclides Particulates/Dust (organic/ inorganic totals)
Emissions of Complex Effluents	Complex Mixtures of Effluents Microorganisms
Emissions of Energy	Noise Heat Electromagnetic Radiation
Nonpollutant Factors	Land Usage Water Usage Soil Stability Aesthetics

Increasing recognition of public health and environmental problems associated with combustion of coal and the attendant government regulations, coupled with economic problems like inflation and severe price increases on imported oil, has led to reexamination of coal technologies utilized in the production of energy. Conventional coal combustion systems are being upgraded and retrofitted with pollution control equipment, i.e., scrubbers, to comply with stationary source emission standards. The newly emerging combustion technologies have some inherent advantages over conventional coal combustion processes and will render much of the older equipment obsolete. One of the most promising coal energy technologies is fluidized bed combustion (FBC) of coal. This particular technology is a combination of the invention and development of 1) pulverized coal for firing in utility boilers and 2) Fritz Winkler's Fluidized Bed Combustor. Although both developments occurred in 1921, they were not immediately combined. Pulverized coal rapidly became widely used in the utility industry, whereas FBC of coal did not receive extensive research and development until the 1950's.

The combination of the two processes did not occur at the time of their invention because the preexisting solid bed coal combustors were readily modified to handle pulverized coal. Also, Winkler's FBC invention was developed in a different context, which was to produce fuel gas by partial combustion of coal. Recently, spurred by restrictive regulations on sulfur dioxide (SO_2), nitrogen oxides (NO_x), and particulate emissions, FBC of coal research and development has gained momentum. The FBC process is well suited to burn high sulfur coal without producing high SO_2 and particulate emissions in the flue gas.

The FBC process combusts coal (or other fuel) at a temperature of 800° to 900°C (1,500° to 1,700°F), in a bed of granular non-combustible material fluidized by air. The bed is made up of granulated dolomite and/or limestone, which absorb the sulfur to a level where the boiler flue gas sulfur dioxide emissions are reduced below the minimum required by regulations. Particulate matter is controlled by electrostatic precipitators or baghouses. Heat from the fluidized bed is transferred to coils immersed in the bed, and water is converted to steam as it is pumped through the coils. The pressurized steam is used either to drive turbines to generate electricity or provide heat for various processes, or is used for other purposes.

This section discusses FBC's major processes, possible environmental contaminants, and applicable pollution control technologies.

PROCESS DESCRIPTION

Basic Principles

For effective combustion of solid fuels, a combustor designer can manipulate three major interrelated variables by which adequate contact is achieved between solid fuel and oxygen, by providing (Farmer et al., 1977):

- Large solid fuel surface area

- Long contact time between gas and solid particles
- High relative speed between gas and solid particles, so that fuel is not shielded from oxygen by a thick layer of stagnant burned gases.

Combustion in a conventional spreader stoker emphasizes the second and third of these variables, while pulverized coal firing depends chiefly on the first and third. Combustion in a fluidized bed can take advantage of all three variables, thus achieving an unusually high intensity of heat release in a small combustion volume.

Basically, a "fluidized bed" combustor consists of a chamber in which granular, non-combustible particles are suspended by air forced through the "bed" from the bottom of the chamber containing holes in the floor. The mass is called "fluidized," because, under proper air pressure and flow rates, the bed exhibits characteristics of a boiling liquid (Yaverbaum, 1977). Depending on the purpose of the combustor, the chemical composition of the fuel, and environmental constraints, the bed material can be inert (i.e., sand), chemically reactive (limestone), or a mixture of materials. Pulverized coal particles are injected into the fluidized mass at a constant rate to maintain a two to five percent fraction of carbon in the bed mass.

When the fuel is fired, the heat is transferred to the non-combustible particles which transfer the heat by conduction to the boiler tubes immersed in the "fluidized bed." The process of conduction rather than convection permits higher rates of heat transfer than a conventional pulverized coal combustor. FBC pilot plants have achieved heat transfer rates ten times higher than conventional combustors. Heat transfer rates of over 100,000 Btu/hr/ft^3 of expanded bed volume or about 50,000 to 60,000 Btu/hr/ft^3 of firebox have been recorded. A typical pulverized coal combustor generates about 20,000 Btu/hr/ft^3 of firebox. Consequently, FBC boilers up to about 250,000 lb. steam/hr can be designed small enough for package shipment by rail. By comparison, a conventional boiler that can be package-shipped by rail can generate only about 50,000 lb. steam/hr. This package feature should make the future erection cost of large-sized FBC boilers significantly lower than for corresponding field-erected stoker-fired or pulverized coal-fired units.

Efficient heat generation and transfer means that FBC units can operate at lower temperatures--about 650° to 950°C (1,200° to 1,800°F)--than conventional pulverized coal combustion units, which operate at 1,400°C (2,500°F) and higher. At these lower temperatures significant amounts of NO_x are not generated. With additional attention to design, NO_x production can be further minimized.

Addition of a chemically active bed material can serve to lower gaseous emissions of other pollutants by trapping them in the bed. For example, high-sulfur, coal-burning, conventional pulverized coal combustion units require extensive, expensive, and often unreliable flue gas desulfurization systems to remove SO_2 from the waste gas stream to meet current emission standards. FBC units, by chemically trapping the sulfur in the bed during combustion, produce an easily handled stable solid. In a simple form, the sulfur trapping reaction can be described as:

$$MeO + 1/2\ O_2 + SO_2 \rightleftharpoons MeSO_4 \qquad (1)$$

MeO (the sorbent) represents a metal oxide chosen for desirable physical and chemical properties and for economic reasons. Bed conditions are maintained to favor sulfation of the metal oxide to form the metal sulfate. The metal oxide-sorbent-feed rate is determined in accordance with the sulfur content of the fuel, the reactivity of the metal oxide, and the emission standards. The sulfur removal is sufficient so that further treatment is not needed.

Another valuable characteristic of FBC technology is its wide tolerance to type and quantity of solid fuels. Caking and non-caking coals, cokes and chars, and solid wastes can all be burned efficiently in a fluidized bed. It is anticipated that FBC boilers will be effective burners for direct combustion of anthracite culm and low-Btu oil shale.

One of the main operating parameters is uniform introduction of fuel and SO_2 acceptor at multiple points within the bed, with generally one fuel/acceptor feed point specified for about ten square feet of bed area. Not only is the average bed temperature relatively low, but temperatures throughout are uniform if good fluidization is maintained. The absence of hot spots means that fuels having low-softening point ash, can be effectively burned without serious ash fusion or clinker formation.

While the FBC concept is relatively simple, the design of a practical, operating unit can be complex. One of the major problems is scaling up design parameters from laboratory and pilot plant sizes to full-scale combustors. At least nine physical parameters/variables influence the design and thereby the efficiency and pollutant output: bed depth, bed and boiler tube geometry, fluidizing grid design, sorbent and coal particle size, fluidization velocity, excess air feed rate, fuel feed mechanism, pressure and temperature. Other variables introduced through government regulations prescribe certain operational modes and pollutant controls, sorbent preparation economics, solid waste disposal, and tax incentives and disincentives.

Consideration of these variables has promoted the development of FBC process design variations. The major design variants are:

- Combustor operating at or near atmospheric pressure in the combustion chamber--basic application is in smaller sizes, primarily for generation of industrial process or space heat or steam.

- Pressurized combustor operating at several atmospheres of pressure--most promising for electrical utilities; power is generated through the expansion of high pressure off-gases flowing through a turbine; the efficiencies are five to ten percent higher than those of the atmospheric FBC units.

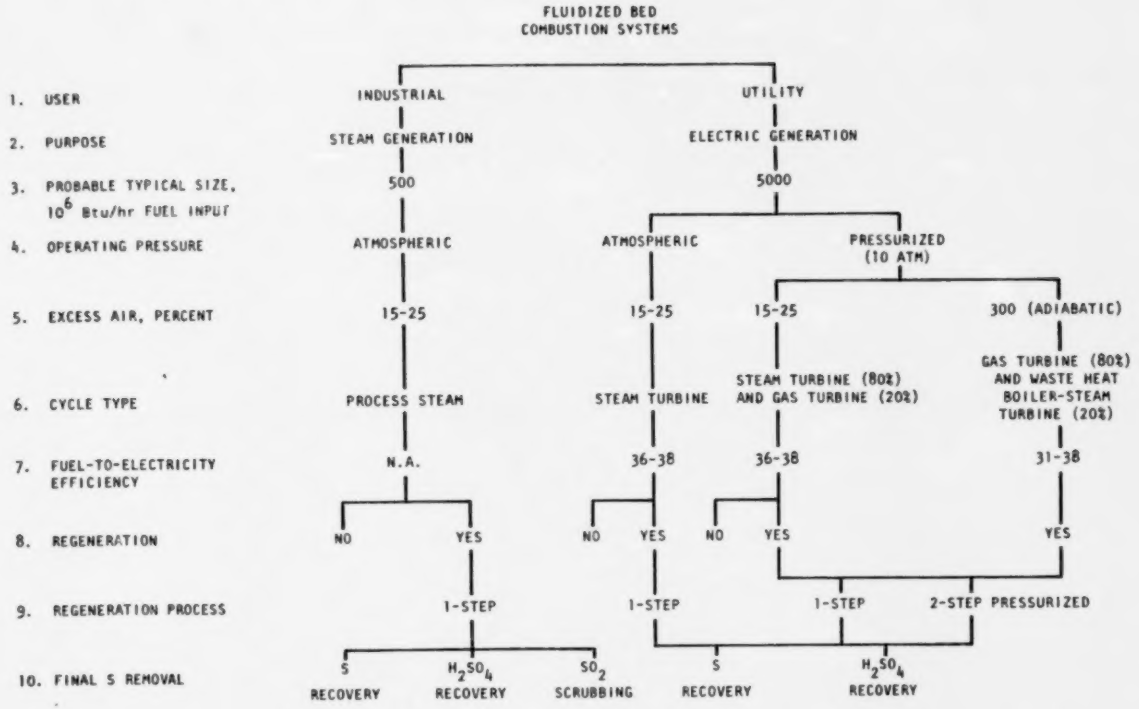
- Absence of cooling units in the bed--Columbus Battelle Laboratory's researchers envision an FBC design where the heat transfer tubes are located outside rather than inside the fluidized bed; benefits include decoupling of combustion and heat exchange processes, reduction in combustor size, reduction of corrosion in the heat exchanger tubes, and improvement of load response.

- High fluidizing air volumes--in this mode, excess air under pressure rather than boiler tubes is used to extract the heat of combustion; electricity is generated by flue gas turbines followed by waste heat recovery units.

- Regeneration of the metal oxide sorbent--regeneration of sorbent material minimizes the solid waste problem and produces a potentially marketable product.

Figure 2 shows several selected FBC system options.

Based on current development efforts, the two major categories of FBC processes are Atmospheric Fluidized Bed Combustion (AFBC) and Pressurized Fluidized Bed Combustion (PFBC), both chemically active. The literature and researchers have treated a number of the AFBC and PFBC variants as separate major categories, e.g., Pressurized, Combined Cycle FBC of coal (adiabatic combustor) (Abelson and Lowenbach, 1977).


FLUIDIZED BED COMBUSTION SYSTEMS
1. USER
2. PURPOSE
3. PROBABLE TYPICAL SIZE, 10^6 Btu/hr FUEL INPUT
4. OPERATING PRESSURE
5. EXCESS AIR, PERCENT
6. CYCLE TYPE
7. FUEL-TO-ELECTRICITY EFFICIENCY
8. REGENERATION
9. REGENERATION PROCESS
10. FINAL S REMOVAL
INDUSTRIAL
STEAM GENERATION
500
ATMOSPHERIC
15-25
PROCESS STEAM
N.A.
NO
YES
1-STEP
S RECOVERY
H_2SO_4 RECOVERY
SO_2 SCRUBBING
UTILITY
ELECTRIC GENERATION
5000
ATMOSPHERIC
15-25
STEAM TURBINE
36-38
NO
YES
1-STEP
PRESSURIZED (10 ATM)
15-25
STEAM TURBINE (80%) AND GAS TURBINE (20%)
36-38
NO
YES
300 (ADIABATIC)
GAS TURBINE (80%) AND WASTE HEAT BOILER-STEAM TURBINE (20%)
31-38
YES
1-STEP
2-STEP PRESSURIZED
S RECOVERY
H_2SO_4 RECOVERY

PROBABLE Ca:S MOLE RATIO IN FEED TO COMBUSTION IS 2:1. COAL SULFUR CONTENT MAY BE 4 PERCENT IN INITIAL SYSTEMS. PROBABLE OPERATING TEMPERATURE OF THE MAIN COMBUSTOR IS 850-950°C.

Figure 2. Selected FBC system options.

(Fennelly et al., 1977)

This section will deal primarily with the two major categories of FBC of coal--the Pressurized and Atmospheric.

Atmospheric Fluidized Bed Combustion of Coal

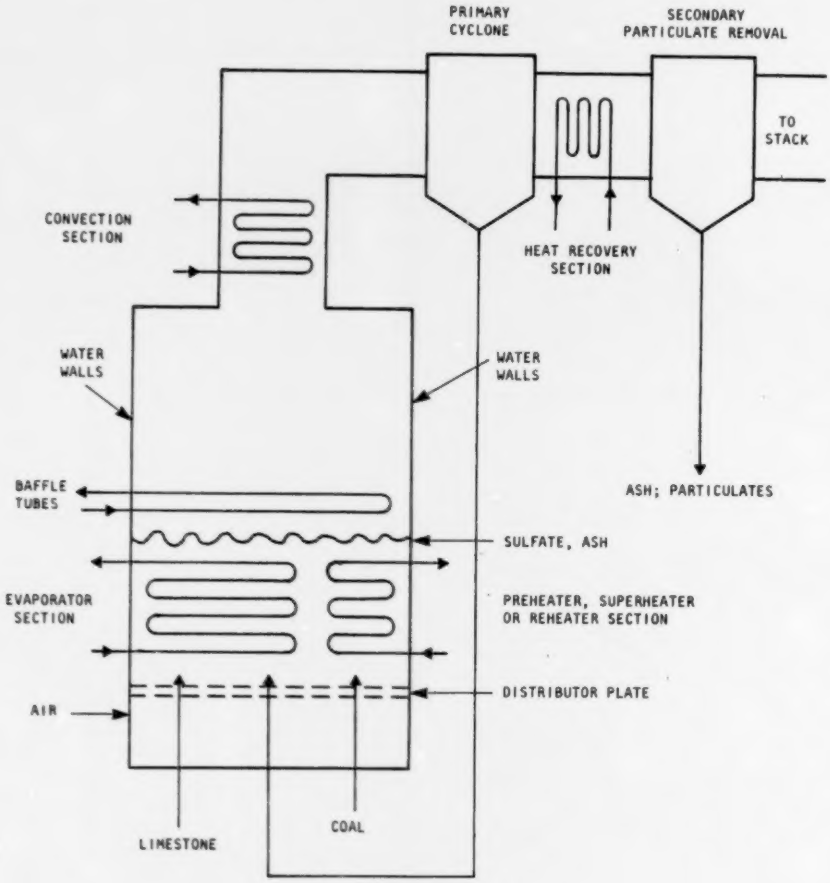
Experts agree that AFBC units will establish themselves in the market first to meet industrial needs for power and steam. The major breakthroughs will be in retrofitted and converted units (Patterson and Griffin, 1978). Babcock Contractors Inc. (Pittsburgh, Pa.) and Riley Stoker Corp. (Worcester, Mass.) entered in a joint agreement in 1978 to manufacture and market AFBC boiler units in the United States. The first commercial units are expected to be operating in late 1979 in Ohio.

Figure 3 is a schematic diagram of an atmospheric pressure FBC boiler (Farmer et al., 1977). The bed consists of a mixture of crushed limestone, dolomite or other inert material, and large ash particles. This mixture is "fluidized" by a stream of air or combustion-gases rising through the supporting grid beneath the bed. Original particle size of the bed material is about 1/8" diameter. The gas velocity is maintained so that the bed particles are suspended and move about in random motion, but do not blow away. Under these conditions, a gas/solids mixture behaves much like a boiling liquid (e.g., seeks its own level, and can be readily moved through channels). The boiler tubes submerged in the bed remove heat at a high rate so that typical bed temperatures are in the range of 750° to 870°C (1,400° to 1,600°F).

Crushed coal (1/4" to 1/2" particles) and the required bed makeup material are continuously added at fuel injection points. Within the bed, the coal burns very quickly, and the bed generally contains less than two-to-four percent carbon. Most of the ash resulting from combustion of the coal is in relatively small, light particles which are swept out of the bed by the flue gas. If high sulfur coal is being burned, sulfated bed material is continuously withdrawn to maintain bed volume and activity for sulfur capture. If low sulfur fuel is being burned, it is assumed that the bed can be composed of inert material, such as alumina or sand, and that bed makeup and withdrawal rates will be very low or negligible.

FBC can effectively control emissions from high-sulfur fuels. For this purpose, the sorbent bed is made up of limestone, dolomite, or lime. Assuming a limestone feed, the first reaction at bed temperature is calcination:

$$CaCO_3 \underset{\Delta}{\rightleftarrows} CaO + CO_2 \qquad (2)$$


PRIMARY CYCLONE
SECONDARY PARTICULATE REMOVAL
TO STACK
CONVECTION SECTION
HEAT RECOVERY SECTION
WATER WALLS
WATER WALLS
ASH; PARTICULATES
BAFFLE TUBES
SULFATE, ASH
EVAPORATOR SECTION
PREHEATER, SUPERHEATER OR REHEATER SECTION
DISTRIBUTOR PLATE
AIR
LIMESTONE
COAL

Combustion Pressure - close to atmospheric (usually balanced draft)
Bed Temperature - 1400 to 1600 F
Gas Velocity - 2 to 12 ft/sec
Bed Material - limestone or dolomite, or inert material for low sulfur fuels not requiring sulfur capture
Fuel - coal, fuel oil, bark and wood wastes, coke, char, etc.

Figure 3. Schematic diagram of atmospheric pressure FBC boiler.

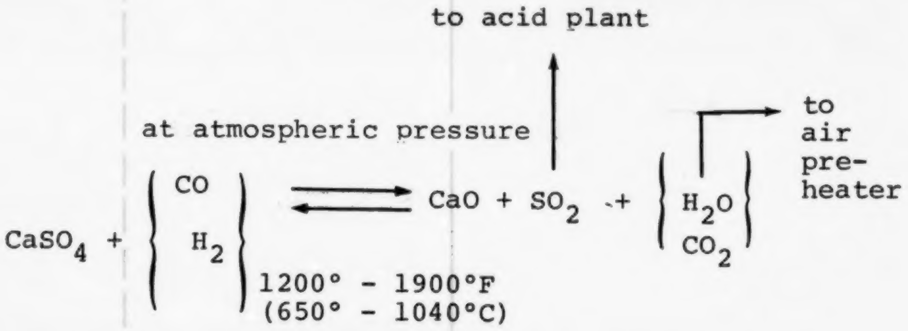
The sulfur in the fuel burns to sulfur dioxide, and bed conditions are maintained to favor sulfation of the lime to gypsum:

$$CaO + SO_2 \underset{\Delta}{\rightleftharpoons} CaSO_4 \qquad (3)$$

The limestone sorbent feed rate is set in accordance with the sulfur content of fuel, and sufficient cleanup of SO_2 is achieved so that no further treatment is required for compliance with sulfur emission regulations. By contrast, a stoker or pulverized-coal-fired boiler emits most of the sulfur in the fuel as SO_2, and high sulfur fuels cannot be burned in these boilers without desulfurization of the flue gas using some sort of scrubber.

Considerable work is underway to develop sorbent regeneration. The incentive for this is to reduce the requirements for fresh limestone or dolomite, and to reduce spent stone disposal costs. In the sorbent regeneration process, the sulfur absorbed by the stone will be released as a more concentrated stream of SO_2, and subsequent disposition of this stream will be by conversion to sulfur or to sulfuric acid.

The basic reactions in the regeneration process are (Newby and Keairns, 1977):



$$CaSO_4 + \left\{\begin{matrix} CO \\ H_2 \end{matrix}\right\} \underset{\substack{1200° - 1900°F \\ (650° - 1040°C)}}{\rightleftharpoons} CaO + SO_2 + \left\{\begin{matrix} H_2O \\ CO_2 \end{matrix}\right\} \qquad (4)$$

The reducing gases are produced by the incomplete combustion of coal.

The regenerator off-gas enriched with SO_2 is piped to the acid plant for removal of particulate matter. This regeneration process is called reductive decomposition and, based on performance and cost criteria, is the most favorable for atmospheric FBC processes (Newby and Keairns, 1977).

The above reactions of the sorbent regeneration process represent an idealized chemical process without the consideration of the presence of other active constituents in the system such as ash. Sorbent regeneration, as an integral component of the FBC technology, provides two essential advantages: 1) minimizes environmental impact by recycling the sorbent and removing SO_2, 2) enhances the technology's economics by reducing the need for raw materials and producing sulfur, a saleable product. However, it is questionable whether the first commercial-scale AFBC units will incorporate sorbent regeneration. The state-of-the-art of FBC processes is rapidly advancing but sorbent regeneration research and development lags behind. Although new uses for sulfur are being continuously developed (i.e., new batteries and as an asphalt additive) overproduction of sulfur is a possibility and may change the sulfur recovery economics.

Pressurized Fluidized Bed Combustion of Coal

Current projections show the PFBC of coal processes to be costly, with costs increasing as units decrease in size. PFBC units are expected to be commercialized for power utility applications, probably in co-generation applications and as large utility boilers. The PFBC processes have a much greater range of operating conditions, higher gas turbine pressures, alternative combustor temperature ranges, and higher excess air levels. This greater process flexibility makes PFBC more applicable for large-scale electrical power generation installations. Although full-scale commercialization of PFBC is not expected until 1990, significant R&D efforts are currently underway to develop these processes.

A schematic diagram of a pressurized FBC boiler (with sorbent regeneration) is given in Figure 4 (Farmer et al., 1977). The higher operating pressures of PFBC achieve higher thermodynamic efficiencies for electric power generation than is possible with an AFBC pressure unit. This is accomplished by use of a combined cycle, generating power from both a steam-driven turbo-generator and a gas turbine. The combustor typically operates at a pressure on the order of ten atmospheres and at temperatures ranging from 900° to 1,040°C (1,650° to 1,900°F). Air is compressed into the combustor, and coal and limestone are injected through lock hoppers. Because of the higher pressure, combustion intensities are even higher than with AFBC, and deeper fluidized beds can be used. Hot effluent flue gas from the boiler is cleaned to reduce the particulate loading to a very low level, and then expanded through the gas turbine to generate supplemental electricity. High temperature particulate removal is currently a major research area.

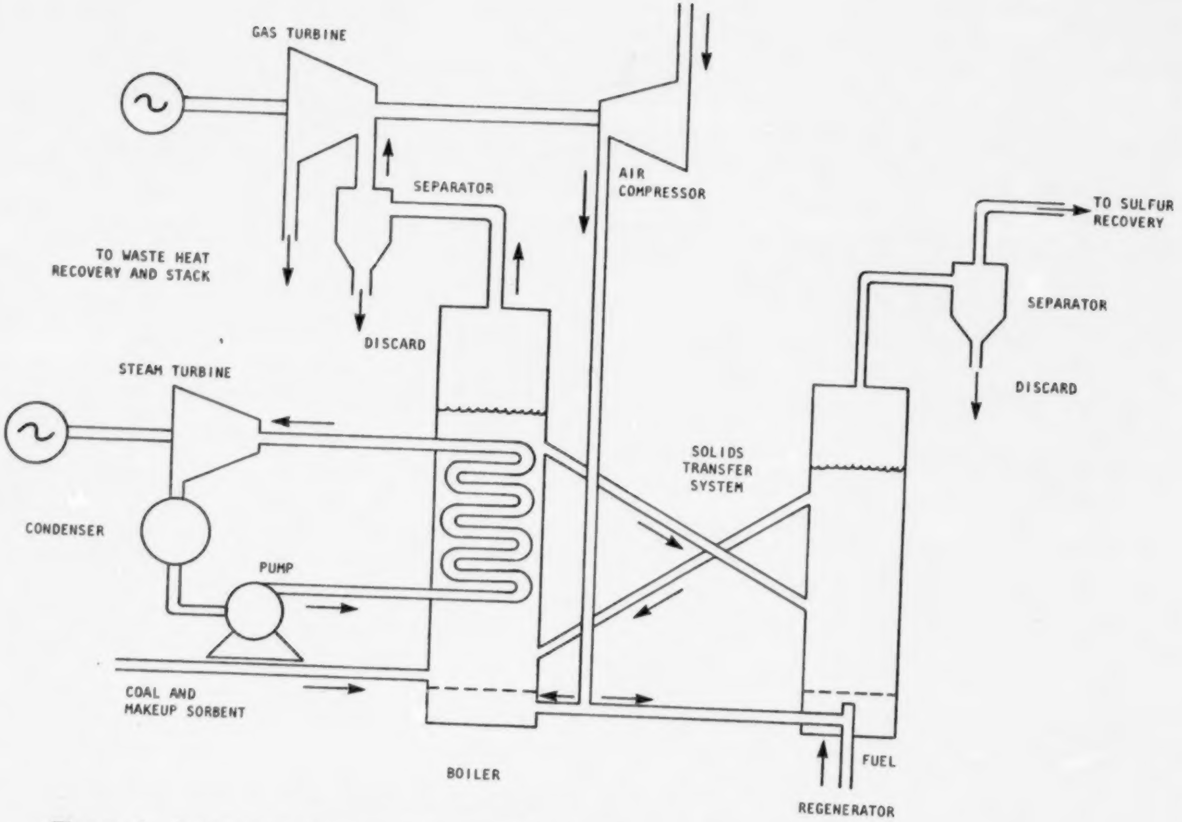

GAS TURBINE
AIR COMPRESSOR
SEPARATOR
TO WASTE HEAT RECOVERY AND STACK
DISCARD
STEAM TURBINE
CONDENSER
PUMP
COAL AND MAKEUP SORBENT
BOILER
SOLIDS TRANSFER SYSTEM
TO SULFUR RECOVERY
SEPARATOR
DISCARD
FUEL
REGENERATOR

Figure 4. Schematic diagram of pressurized FBC boiler with sorbent regeneration.

PFBC gives significantly lower SO_x emissions than the atmospheric version when burning high-sulfur coal.

The applicable sorbent regeneration process is a two-step reaction of sulfate reduction to sulfide followed by reaction with steam to generate H_2S (Newby and Keairns, 1977):

$$\text{(1)}\quad CaSO_4 + H_2 + 3CO \underset{\substack{8\text{ atm}\\ 1500°\text{F}\\ (876°\text{C})}}{\rightleftharpoons} CaS + H_2O + 3CO_2 \tag{5}$$

$$\text{(2)}\quad CaS + CO_2 + H_2O\ \text{(steam)} \underset{\substack{12\text{ atm}\\ 1100°\text{F}\\ (593°\text{C})}}{\rightleftharpoons} \underset{\substack{\downarrow\\ \text{reuse}}}{CaCO_3} + \overset{\substack{\text{to acid plant}\\ \uparrow}}{H_2S} \tag{6}$$

The H_2S rich gas is fed to an acid plant for extraction of sulfur.

There are a number of different sorbents; however, based on thermodynamic projections of desulfurization and regeneration performance, dolomite and limestone (CaO/MgCa $[CO_3]_2$ $CaCO_3$) appear to be the best and most cost-effective choices for AFBC (Newby and Keairns, 1977). Table 3 shows the alternative sorbents and their projected potential.

ENVIRONMENTAL POLLUTANTS FROM FBC OF COAL

Methods of Determining Pollutants

Theoretical and empirical methods can be used to determine what pollutants will be generated from fluidized bed combustion of coal. At this stage of FBC development, however, both methods provide only approximations for future commercial-scale FBC facilities.

The theoretical method involves the calculation of a materials balance for all the process streams of the FBC of coal. The materials balance concept is based on the law of conservation of matter which states that atoms are neither created nor destroyed, except in nuclear reactions. The appropriate equations for any system are:

TABLE 3. ALTERNATIVE SORBENT SELECTION
(Newby and Keairns, 1977)

Sorbent	Desulfurizer potential		Reduction Decomposition potential		2-Step regeneration potential		Availability potential	Cost potential	Overall
	Atmospheric	Pressurized	Atmospheric	Pressurized	Atmospheric	Pressurized			
Na_2CO_3	Limited temp. range	No	Limited SO_2	No	Good	No	Good	--	Limited applicability; highly corrosive nature
CaO	Good	Good	Good	Limited SO_2	Limited H_2S	Good	Good	Good	Good potential
$SrCO_3$	Good	Good	No	No	Good	Good	Poor	--	Poor availability
$BaCO_3$	Good	Good	No	No	Good	Good	--	--	Reasonable potential
$LiAlO_2$	Good	Good	Good	Limited SO_2	Good	Good	--	Poor	Poor cost potential
$LiFeO_2$	Good	Good	Good	Limited SO_2	Limited H_2S	Limited H_2S	--	Poor	Poor cost potential due to limited performance
Li_2TiO_3	Good	Good	Limited SO_2	No	Good	Good	--	Poor	Poor cost potential
$NaAlO_2$	Limited temp. range	No	Good	No	Good	No	Good	--	Limited applicability; highly corrosive nature
$NaCO_3 \cdot Fe_2O_3$	Limited temp. range	No	Limited SO_2	No	Good	No	Good	--	Limited applicability; highly corrosive nature
$CaAl_2O_4$	Good	Good	Good	Good	Good	Good	Good	Good	Reasonable potential
$SrAl_2O_4$	Good	Good	Good	Good	Good	Good	Poor	--	Poor availability
$SrTiO_3$	Good	Good	Good	Good	Good	Good	Poor	--	Poor availability
$BaAl_2O_4$	Good	Good	Good	Good	Good	Good	--	--	Reasonable potential
$BaTiO_3$	Good	Good	Good	Good	Good	Good	--	--	Reasonable potential

$$\begin{array}{c} \text{Accumulation of} \\ \text{atomic species J} \\ \text{within the system} \end{array} = \begin{array}{c} \text{total atomic} \\ \text{species J entering} \\ \text{system} \end{array} - \begin{array}{c} \text{total atomic} \\ \text{species J} \\ \text{leaving system} \end{array} \qquad (7)$$

By summation of all atomic species, the materials balance is calculated

$$Ma = Me - M\ell \qquad (8)$$

where:

Ma = total mass accumulating in system
Me = total mass entering the system
$m\ell$ = total mass leaving the system

The materials balance takes into consideration the nature and composition of coal and the sorbent materials and the chemical reactions and thermodynamics of the process. This approach cannot account for all the changes in operating conditions in a commercial-size process and subsequent differences in chemical reactions and thermodynamics producing different system by-products.

For most elements, the information available will not permit such calculations. First, the necessary data are either not recorded or go unreported. In addition, spark source mass spectrometry (SSMS) as commonly used is notoriously unreliable. In one case, a 40 percent relative standard deviation was reported (Carpenter et al., 1978) and in another, values were reported to be within an order of magnitude, leading to mass closures varying from zero to 1,000 percent (Pillai and Roberts, 1977). With appropriate care and the proper analytical technique, usually atomic absorption, closure values nearing 100 percent can be obtained even for the volatile trace elements (Pillai and Roberts, 1977). For the initial Battelle work, "The emphasis . . . . was mainly on establishing a general methodology for comprehensive sampling--analysis from FBC units and not to define the precision and/or accuracy of the techniques employed" (Merryman et al., 1977). This emphasis is apparent through all Level 1 analyses.

The second approach is empirical. Bench scale, pilot plant, and demonstration plant test data on environmental contaminants can be compiled and extrapolated to fit commercial-scale facilities. However, the environmental contaminant data from existing experimental FBC projects are highly variable and not necessarily representative of a commercial-scale operation. The amount and nature of test data obtained under closely controlled conditions from special purpose projects can completely misrepresent the FBC process when extrapolated to a commercial size facility.

Combining the theoretical and empirical methods will overcome some of their shortcomings and can provide a reasonably sound basis for predicting what environmental contaminants can be expected from commercial-scale FBC processes.

Sources and Major Types of Pollutants

The major sources of pollutants are the principal unit operations of the FBC process. They are listed below, with their associated major pollutants:

- Sorbent (limestone) preparation and feed unit operations
  - air emissions (fine particulates)
  - leachates
- Fuel preparation - coal storage, drying, crusting, and feeding unit operations
  - air emissions (particulates, fugitives)
  - leachates
  - solid wastes (pyrite)
- Coal combustion in fluidized bed unit operations
  - air emissions (SO_2, NO_x, particulates, HC_x, trace elements)
  - solid wastes (ash leachates, fugitive emissions)
- Sorbent regeneration unit operations
  - spent sorbent discard
  - by-products (sulfur recovery - acid plant)
- Steam turbine and water treatment unit operations
  - thermal discharges (air and water)
  - liquid discharges
  - sludge
- Air pollution control unit operations
  - steam
  - flue gas emission (particulates, trace elements, HC_x)
  - solids (sludge, ash)

Figure 5 is a schematic of the major unit operations of a generic FBC process; major process waste streams are numbered and identified in Table 4. Figure 6 is a generic process flow of AFBC of coal and the associated environmental waste streams. While PFBC of coal process flows are generically similar to AFBC, the thermodynamics of the two processes differ markedly due to the pressurization of the fluidized bed combustion chamber and the higher system flow rates.

TABLE 4. STREAM DESIGNATIONS FOR GENERIC UNITS
(Abelson and Lowenbach, 1977)

Stream No.	Designation
1	Stack Gas
2	Particulate Removal Discard
3	Bed Solids Discard
4	Particulate Removal Discard--Regeneration Operations
5	Other Effluents from Regeneration and Sulfur Recovery Operations
6	Blowdown from Steam Turbine Cycle
7	Blowdown from Water Treatment Operations
8	Product from Sulfur Recovery (Sulfur or Sulfuric Acid)
9	Raw Fuel to Preparation
10	Raw Sorbent to Preparation
11	Intake Water to Treatment
12	Air to Combustor
13	Air/Steam to Regenerator
14	Prepared Fuel Feed to Combustor
15	Prepared Fuel Feed to Regenerator
16	Start-Up Fuel Feed
17	Prepared Sorbent Feed to Combustor
18	Bed Solids to Regenerator
19	Flue Gas to Particulate Removal
20	Makeup Water to Steam Turbine Cycle
21	Recycle from Particulate Removal
22	Recycle from Regeneration and Sulfur Recovery
23	Gas to Gas Turbine Inlet (Pressurized FBC Only)

Environmental Pollutants

Based on the analysis of the raw coal, numerous potential pollutants can be predicted and their concentration ranges in waste streams estimated. Fennelly et al. (1977), in calculating the potential pollutants from FBC processes, categorized the potential pollutants into the following major categories:

- Acids and Acid Anhydrides
  - Organic Acids - Compounds such as carboxylic acids, dicarboxylic acids, and sulfonic acids could conceivably form from incomplete combustion of hydrocarbons; however at the

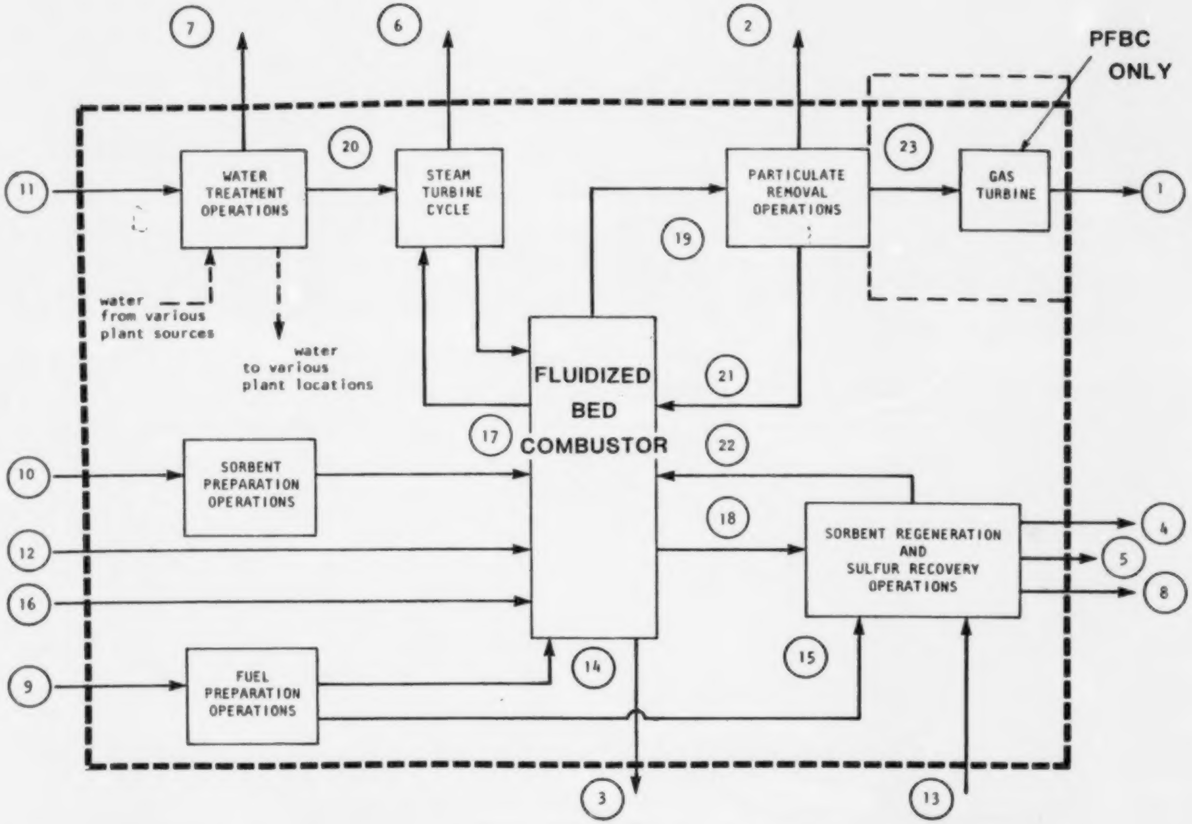

PFBC ONLY
WATER TREATMENT OPERATIONS
STEAM TURBINE CYCLE
PARTICULATE REMOVAL OPERATIONS
GAS TURBINE
water from various plant sources
water to various plant locations
FLUIDIZED BED COMBUSTOR
SORBENT PREPARATION OPERATIONS
FUEL PREPARATION OPERATIONS
SORBENT REGENERATION AND SULFUR RECOVERY OPERATIONS
1
2
3
4
5
6
7
8
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Figure 5. Generic schematic of FBC unit operations with numbered process flows producing waste streams.

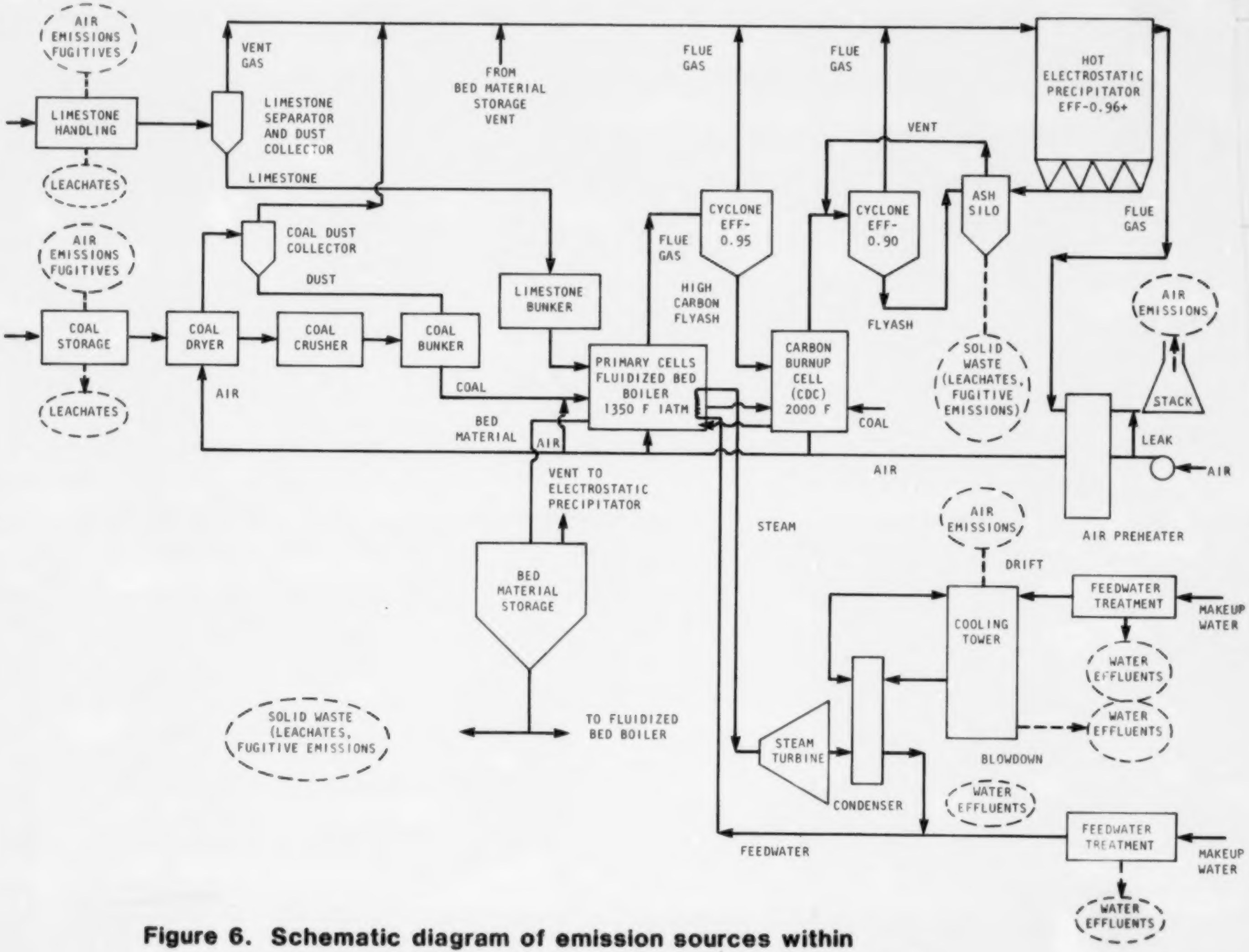
AIR EMISSIONS FUGITIVES
LIMESTONE HANDLING
LEACHATES
AIR EMISSIONS FUGITIVES
COAL STORAGE
LEACHATES
VENT GAS
LIMESTONE SEPARATOR AND DUST COLLECTOR
LIMESTONE
COAL DUST COLLECTOR
DUST
COAL DRYER
AIR
COAL CRUSHER
COAL BUNKER
COAL
FROM BED MATERIAL STORAGE VENT
LIMESTONE BUNKER
BED MATERIAL
AIR
PRIMARY CELLS FLUIDIZED BED BOILER 1350 F IATM
FLUE GAS
FLUE GAS
CYCLONE EFF-0.95
HIGH CARBON FLYASH
VENT TO ELECTROSTATIC PRECIPITATOR
BED MATERIAL STORAGE
TO FLUIDIZED BED BOILER
SOLID WASTE (LEACHATES, FUGITIVE EMISSIONS)
FLUE GAS
VENT
CYCLONE EFF-0.90
FLYASH
CARBON BURNUP CELL (CDC) 2000 F
COAL
ASH SILO
SOLID WASTE (LEACHATES, FUGITIVE EMISSIONS)
HOT ELECTROSTATIC PRECIPITATOR EFF-0.96+
FLUE GAS
AIR EMISSIONS
STACK
LEAK
AIR
AIR
AIR PREHEATER
STEAM
AIR EMISSIONS
DRIFT
COOLING TOWER
FEEDWATER TREATMENT
MAKEUP WATER
WATER EFFLUENTS
WATER EFFLUENTS
BLOWDOWN
STEAM TURBINE
CONDENSER
WATER EFFLUENTS
FEEDWATER
FEEDWATER TREATMENT
MAKEUP WATER
WATER EFFLUENTS

Figure 6. Schematic diagram of emission sources within atmospheric-pressure fluidized bed combustion plant.
(Henschel, 1977)

temperatures involved (~850°C), compounds of this type should quickly decompose to form small hydrocarbons and CO_2.

- Inorganic Acids - The predominant inorganic acids should be HCl and HF. Sulfuric, sulfurous, nitric and nitrous acid should not form until the flue gas has cooled to temperatures less than 240°C.

- Carbon Compounds

The major carbon compounds, as expected, will be CO_2 and CO. Soot (solid carbon) could be a problem since it would be emitted as small particles (<0.1μm) which could pass through most particulate control devices. Calcium and magnesium carbides could also form in small quantities in the ash formed in the combustor, the carbon burn-up cell or the regenerator. After ash disposal, these compounds could release acetylene upon contact with water. The quantities generated, however, should pose no special problems.

- Halogen Compounds

Halogens should be emitted primarily as HX (where X = F, Cl, Br). Experience in coal combustion chemistry indicates that the presence of chlorine in coal enhances condensation reactions via elimination of HCl; hence, species such as chlorinated hydrocarbons are not favored. Furthermore, most chlorinated aliphatics are unstable at the temperatures prevailing in the combustor.

- Hydrocarbons

Long chain aliphatics and cyclic hydrocarbons should decompose within the bed to form H^2 and smaller hydrocarbons. Some of these smaller hydrocarbons could condense to form polycyclic species such as pyrene, anthracene, etc. Hydrocarbon concentrations are strongly dependent on the amount of excess air. With excess air levels of about 20 percent, total hydrocarbon levels (measured as methane) of less than 100 ppm are attainable. Based on a comparison with data from conventional combustion systems, 1 ppb of benzo(a)pyrene (or similar compounds) could be present in fluidized bed combustion. With excess air levels of 10 percent, benzo(a)pyrene could reach 10 ppb.

- Nitrogen Compounds

  The predominant nitrogen compound should be NO. Trace amounts (< ppm) of HCN, $(CN)_2$ and azoarenes may be present. Species such as amines, pyridine, pyrroles, and nitrosamines, which could form as combustion intermediates, should quickly decompose within the bed to form hydrocarbons, NO and HCN.

- Oxygen Compounds

  Oxygenated hydrocarbons such as furans, ethers, esters, aldehydes, etc. could form as combustion intermediates. These species, however, are unstable at temperatures on the order of 850°C, and they should decompose before escaping from the bed. Ozone, if formed, would also decompose at these temperatures.

- Particulates

  . . . Although there are only very limited data available on particulate concentrations and particle size distributions, it seems that no special problems should result from particulate loadings, provided the conventional process cyclones and a control device such as an electrostatic precipitator or a fabric filter are used. The actual performance of these devices on full-scale fluidized bed boilers, however, has not yet been tested.

- Radioactive Isotopes

  Based on a "worst case" analysis with lignite coal, uranium could be emitted at significant levels, but the radioactive isotopes of uranium as well as those of other radioactive elements should not be present in high enough quantities to cause concern. [See Table 5 for actual measurements.]

- Sulfur Compounds

  SO_2 and SO_3 will be the major sulfur compounds formed. The presence of limestone in the bed, however, should keep these emissions below present emission standards. COS could form in trace quantities (~1 ppm). Compounds such as thiophenes or mercaptans, if formed as combustion intermediates, will decompose to hydrocarbons and H_2S; the H_2S will then be oxidized to form SO_2.

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TABLE 5. RADIOACTIVITY MEASUREMENTS[a]

Sample description	Radioactivity pico Curies/gm α	Radioactivity pico Curies/gm β
Test 6/1[a]		
Bed material	18.8 ± 4.0	46.8 ± 6.0
Coal	5.0 ± 2.4	9.0 ± 5.2
Dolomite	5.8 ± 2.4	8.2 ± 5.2
Primary cyclone dust	8.2 ± 3.2	44.4 ± 6.0
Secondary cyclone dust	14.8 ± 4.0	69.4 ± 6.6
Test 6/2[a]		
Bed material	8.2 ± 3.2	24.6 ± 5.4
Coal	10.6 ± 3.2	16.0 ± 5.4
Dolomite	2.4 ± 2.4	27.4 ± 5.4
Primary cyclone dust - coarse	19.6 ± 4.0	55.0 ± 6.4
- fine	9.0 ± 3.2	61.2 ± 6.4
- total	19.4 ± 4.0	55.1 ± 6.4
Secondary cyclone dust - coarse	14.0 ± 4.0	84.6 ± 7.0
- fine	5.0 ± 2.4	94.8 ± 7.2
- total	11.3 ± 3.5	87.7 ± 7.1
Flue gas dust - coarse	22.2 ± 5.0	111.8 ± 7.2
- fine	7.0 ± 7.0	78.9 ± 23.7
Total in flue gas dust	20.7 ± 5.2	108.5 ± 8.9
Total in flue gas pci/kg gas	4.9	25.1
Exxon[b]		
Flue gas	6 ± 3	30 ± 10

[a] Pillai and Roberts, 1977.

[b] Murthy and Henschel, 1978.

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PAGE NUMBER

- **Trace Elements**

  Data should be acquired with respect to the fate of trace elements such as Be, As, Pb, V, Ni and Cl. Also needed are data with respect to chemical composition as a function of particle size. For the most part, the other trace elements commonly encountered in coal combustion are captured in the coarse solids and remain in the bed. The high pH of the bed material is advantageous in that it tends to retard the leaching of the heavier metals.

Fennelly and others have also estimated the expected concentrations in the flue gas and the solid waste. Their estimates follow:

Flue Gas

One hundred parts per million: (100 ppm)	CH_4, CO, SO_2, NO
Ten parts per million: (10 ppm)	SO_3, C_2H_4, C_2H_6, HCl
One part per million: (1 ppm)	HF, HCN, NH_3, $(CN)_2$, COS, H_2S, H_2SO_4, HNO_3, Elemental Vapors, As, Pb, Hg, Br, Cr, Ni, Se, Cd, U Be, Na
One part per billion: (1 ppb)	Diolefins, Aromatic Hydrocarbons, Phenols, Azoarenes
One-tenth part per billion: (0.1 ppb)	Carboxylic Acids, Sulfonic Acids, Alkynes, Cyclic Hydrocarbons, Amines, Pyridines, Pyrroles, Furans, Ethers, Esters, Epoxides, Alcohols, Ozone, Aldehydes, Ketones, Thiophenes, Mercaptans, Chlorinated Hydrocarbons

Flue Gases and Particulates

Table 6 shows the reported ranges for some of the minor flue gas constituents found in FBC research installations. From the results, it appears that PFBC produces less pollutants than AFBC. The combustion efficiency also appears to be greater in pressurized units than in atmospheric, based on the

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TABLE 6. REPORTED RANGES OF SOME MINOR STACK FLUE GAS CONSTITUENTS
(Values in ppm)

Compound or Element	Exxon[a]	Leatherhead[b]	MERC[f]	Battelle[c]	Estimated[d] worst case
SO_3	5[e]	0-4		0.14-18.6	200
Cl^-	33.5-47.1	18		37.3-43.5	10
F^-	6.7-14.5	2.5		0.082-0.70	1
HCN	<0.0004-0.001	2-3.5	<0.05-<0.18	0.07-0.18	1
NH_3	0.06-0.64	0	0.13	1.8-7.05	1
CO	53-130	0	100-400	790-4790[g]	100
HC	3.3[e]	1-13		85-900[g]	CH_4-100 C_2H_4-10
H_2S, COS CS_2, C_2H_4S	<0.1-<6	0	<4.3		4

[a] Allen et al., 1978a.

[b] Pillai and Roberts, 1977.

[c] Merryman et al., 1977.

[d] Fennelly et al., 1977.

[e] Murthy and Henschel, 1978.

[f] Allen et al., 1978b.

[g] Merryman et al., 1978.

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outputs of CO and HC. Chloride output is similar in both types of operation and above the estimated maximum emission.

Fluorine emissions will probably be highly variable depending upon the presence of excess CaO and the stack temperature at particulate clean-up. At operating bed temperatures, fluorine will be released as HF which will then combine with any excess CaO below 550°C and MgO below 450°C in the following reaction:

$$MeO + 2HF \rightleftharpoons MeF_2 + H_2O \tag{9}$$

Argonne National Laboratories noted that fluorine retention was 56 to 62 percent with a calcium sorbent compared to 5 to 23 percent with a sorbent free bed (Alvin et al., 1977).

Table 7 shows collated information on the emission of eight toxic volatile elements found in the flue gas after some small particulate removal. The output of lead is dependent upon several variables, including the tendency of lead compounds to preferentially deposit upon small particulates, the total concentration of chlorine in the system, and pressure. At high temperatures and pressures, gaseous $PbCl_4$ is the thermodynamically favored compound but, at high temperatures and low pressures, gaseous PbO is favored. Upon cooling and/or lowering the pressure, PbO will precipitate out quite rapidly. In addition, conversion of lead to $PbCl_4$ is related to the concentration of chlorine in the gas. If the chlorine concentration falls to 50 percent of its assumed value, then $PbCl_4$ falls to 6 percent of its previous value (Alvin et al., 1977; 1978). In conventional combustion, lead preferentially precipitates upon smaller particulates and there is some evidence that it behaves the same in FBC (see Table 8). Thus, lead emission in the exhaust gas is favored by a low chlorine coal, or, alternatively, a high alkali release which will scavenge the chlorine, and efficient removal of the fine particulates.

Mass balance information permits emission calculations as shown in Table 9. Selenium and mercury behave in fluidized bed operations as they do in conventional combustion, probably because the elemental form in both cases is thermodynamically preferred as in the following reactions:

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(PREVIOUSLY EIN. EPA FORM 287)
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TABLE 7. VOLATILE ELEMENT ANALYSIS IN FLUE GAS[a]

Element	Battelle[b] μg/m^3	MERC[c] μg/m^3	Exxon[d] μg/m^3	Leatherhead[e] ppb
Antimony		<0.27-0.48	1.2-1.5[f]	0.4
Arsenic	0.039	0.12-0.72	0.8-2.1[f]	3.0
Beryllium	<0.026		<0.4	0.6
Cadmium	<0.052		0.1	1.1
Lead	<1.3		<1.2	5.4
Mercury	0.009	0.13-0.51	0.50-1.27[f]	3.9
Selenium	<0.039		<1.4	20
Tellurium	<0.26		<1.7	Trace

[a] All analysis done by atomic absorption or optical emission spectroscopy.

[b] Merryman et al., 1977.

[c] Allen et al., 1978b.

[d] Murthy and Henschel, 1978.

[e] Pillai and Roberts, 1977.

[f] Allen et al., 1978a.

TABLE 8. PROJECTED FLUE GAS EMISSION OF TRACE ELEMENTS AS A PERCENTAGE OF THE ELEMENT ENTERING THE SYSTEM
(Pillai and Roberts, 1977)

	Emissions (% of input)		
Element	Leatherhead	Exxon	Conventional combustion
Mercury	81	80	90 - 100
Selenium	51	-	30[a] - 70[b]
Arsenic	5	15	50 - 60
Lead	10	0 - 20	0 - 60
Cadmium	14	-	75[c]
Tellurium	4	-	50[c]
Beryllium	8	20 - 40	10[c]
Antimony	5	-	75[c]

[a] Andren et al., 1975.

[b] Kaakinen et al., 1975.

[c] DeAngelis and Reznik, 1979.

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TABLE 9. POTENTIAL ENRICHMENT OF ELEMENTS IN THE FINE PARTICULATE CATCH

Element	Class	Morgantown[a]	Morgantown[b]	Battelle[c]	Exxon[d]	Leatherhead[e]	Conventional[f]
Pb	II	I	PE			E	E
Tl		PD	I	PE	PE		
Yb		I	I		PE		
Ho					PE		
Gd		PE			PE		
Eu	I	I	I		PE		N
Nd		I	I		PE		
Pr		PE	I		PE		
Cs	IV			I	PE		
I		PE	I	I	ND		
Te		PD	ND	ND	ND		
Sb	II	I	I			E	E
Sn		I	I	PE	PE		
Cd	II				ND	E	
Nb			I		PE		
Y			I		PE		
Sr	I	I			PE		N
Br	III		PE		PD		G
Se	II		ND	ND			E
As	II	PE	PE			E	E
Ge		PE	PE		PE		
Ga	II	I	I		PE		E
Zn	II	PE	PE				E
Cu	II	PE	PE				E
Ni	IV	PE			PE		S
Co	I	I	PE		I		N
Mn	I	I	I		PE		N
Cr	IV	PE	I		I		S
V	IV	I			PE		S
Sc	I	PE	I		PE		N
Cl	III		I		PD		G
P		PE	I		I		
Na	IV	PE	I		I		S
F		PE	PE		PE		
B		PE		PE	PE		
Be		PE	PE	PE	PE	E	
Li		ND			PE		

[a] Carpenter et al., 1978.

[b] Allen et al., 1978b.

[c] Merryman et al., 1978a.

[d] Allen et al., 1978a.

[e] Pillai and Roberts, 1977.

[f] Klein et al., 1975.

KEY: CLASS I - lithophiles - aluminosilicates - little volatility
II - chalcophile - sulfides - highly volatile
III - gases
IV - unclassified - appear to have properties between Classes I & II.

E - enriched; measured by atomic absorption
G - gas
I - indeterminate
N - not volatile
ND - not determined
PD - probably depleted SSMS
PE - probably enriched SSMS

$$SeO_2 + 2SO_2 \rightleftharpoons Se^o + 2SO_3 \qquad (10)$$

$$H_2SeO + 2SO_3 + H_2O \rightleftharpoons Se^o + 2H_2SO_4 \qquad (11)$$

$$HgCl_2 \underset{\Delta}{\rightleftharpoons} Hg + Cl_2 \qquad (12)$$

From thermodynamic data (Alvin et al., 1977), beryllium would be expected to volatilize without deposition upon cooling, thus showing a high emission. This, however, is not demonstrated by the available data. Also, from the same theoretical evaluation, boron and chlorides would be emitted in a gaseous form. While chloride emissions are higher than expected in some cases, no adequate information is available, nor is any information available for boron.

Arsenic is another element not behaving as predicted from conventional coal combustion. There is some evidence which indicates that it is being preferentially deposited upon small particulates (see Tables 8 and 9). Cadmium, tellurium, and antimony also do not behave as predicted.

Without additional mass balance information, the fate of any element cannot accurately be determined. However, a tentative prediction can be made by establishing a concentration ratio where:

$$(\text{concentration})_x = \frac{(\text{concentration})_x \text{ after combustion}}{(\text{concentration})_x \text{ before combustion}} \qquad (13)$$

After statistically accounting for carbon loss during ignition of the coal, the elemental values of the small particulate catch are compared to their values in the coal, while the spent bed material is compared to the limestone. Simplifying assumptions ignore the contributions of the elements in the limestone and consider that none of the bed material will be carried into the fine particulate catch, while no fly ash remains behind in the bed. (Leachate information supports this with the bed reject leachate having a pH of 12 and the second cyclone leachate having a pH of 9.) The assumptions are, of course, debatable considering that the aluminosilicate-associated elements are not volatile. However, since at FBC operating temperatures these elements do not melt to form a fused slag, they could be carried from the bed as fly ash. Table 9 shows a qualitative description of the available enrichment information. Considering the ambiguities of SSMS, only the most tentative conclusions can be drawn.

Generally, in both pressurized and atmospheric combustion, Class II, sulfide-associated elements behave as expected, based on pulverized coal combustion (PCC) technology. That is, they are initially volatilized and then recondensed on the small fly ash particles. One exception is cadmium which appears to be found in all waste streams. From the Leatherhead data, it would appear that antimony is not released as a gas, contrary to PCC expectations. But it is the only combustor for which data indicate a concentrating effect on the small particulate catch. Thallium, another toxic element appears enriched in one case and depleted in another.

It would also appear that the Class I elements are being removed from the bed, preferentially concentrating on the small particle catch, contrary to their behavior in PCC units. Considering that SSMS is the source of the data, this conclusion may be inaccurate. Alternatively, because of the temperature, the physical behavior of the elements might differ, in FBC units, from PCC units.

Too little data are available to accurately predict the fate of the Class III and IV elements. Superficially, it would appear that there is a difference between Pressurized and Atmospheric FBC units, but more must be known.

To extract additional energy in the PFBC system, the hot exhaust gases will be expanded through a turbine. However, if the gases contain alkali metals, hot corrosion of the turbine blades will likely occur. Sodium-chloride-doped coal and charcoal suggest an inverse emission relationship with ash content (Swift et al., 1977). The scavenging is probably a function of the clay minerals in the coal for which the following reaction is typical:

$$Al_3O_3 \cdot SiO_2 + 5SiO_2 + 2KCl + H_2O \rightleftharpoons 2KAlSi_3O_8 + 2HCL \quad (14)$$

The calculated effect of the aluminosilicate is to suppress about 98 percent of the potassium emissions and about 86 percent of the sodium emissions at 925°C and ten atmospheres (Alvin et al.,1977). In experiments, thermally activated bauxite captured 98 percent of vaporized sodium chloride although alundum ($\alpha - Al_2O_3$) did not trap any salt (Swift et al., 1977). Addition of an aluminosilicate mineral to the bed will probably be necessary in PFBC combustion.

A Level 2 analysis of the second run from the Battelle miniplant has begun characterizing the inorganic compounds found in the flue gas particulates (Table 10). The presence of S^{-2} in the particle interior but not in the surface is noteworthy; it might imply that the center of the particles never reach a complete oxidizing condition. The inability to detect barium and nickel ions in the particulate leachate or by instrumental analysis of the particle is interesting. SSMS data (Merryman et al., 1977) report their presence as "00 and 200 ppm, respectively, in the second cyclone removal system. Perhaps the technology is insufficiently sensitive, SSMS is inappropriate, or the elements are present as insoluble compounds ($BaCO_3$, $BaSO_4$, $NiCO_3$ or NiO).

With the scarcity of information, the inadequacy of the analytical technique and the lack of runs where only a single variable was changed, little can be said about elemental fractionation during different operating conditions. It would be desirable, for example, to have reported information from a series of runs where the only variable was the amount of limestone added for sulfur sorption. It would be expensive but desirable. Considering the economic cost of limestone and the cost of disposal, it is only reasonable to predict that the calcium-to-sulfur ratio of limestone to coal will approach 1.1 to 1. At least two changes from the current conditions can be predicted: less calcium oxide will be present in the waste stream to cause thermal problems upon disposal and less fluoride will be trapped in the small particulate catch as it is now by the excess CaO.

A number of known polycyclic carcinogens have been identified in the flue gas of fluidized bed combustors (Table 11). While solid carbon has not specifically been determined in the coarse dust, carbon concentrations are usually very low (see Table 23) and this is reflected in the low polynucleated aromatic hydrocarbon (PAH) concentration of the removal system. The small particulates of the Battelle AFBC unit have higher concentrations of PAH material. This could reflect the tendency for PAH material to deposit on the fines, a difference between AFBC and PFBC operation, or a difference in stack temperatures at collection. The higher concentrations of PAH material in the flue gas may depend on the same factors as the fine particulates.

TABLE 10. INORGANIC ELEMENTS AND COMPOUNDS IDENTIFIED IN FLUE GAS PARTICULATES
(Ryan et al., 1979)

IR		ESCA					
>27μ	<27μ	>27μ		<27μ			
		Oxidation state	Atom percent	Oxidation state	Atom Percent		
					Surface	Interior 100 Å	Interior 200 Å
$CaSO_4$	SiO_2	Fe^{+3}	2	Fe^{+3}	1	1	2
$CaSO_4 \cdot 1/2H_2O$	$CaSO_4$	O^{-2}	62	O^{-2}	61	53	53
$CaSO_4 \cdot 2H_2O$	$CaSO_4 \cdot 2H_2O$	Ca^{+2}	4	Ca^{+2}	5	10	9
SiO_2		C	-	C	-	-	-
Fe_2O_3		S^{+6}	2	Na^{+1}	2	1	1
Fe_3O_4		Si^{+2}	22	S^{+6}	7	5 SO_4^{-2}, S^{-2} 6:4	3 SO_4^{-2}, S^{-2} 5.5:4.5
		Al^{+3}	8	Si^{+2}	13	16	17
				Al^{+3}	12	16	14

XRD		EMPA		
>27μ	<27μ	Element	Relative abundance %	
			>27μ	<27μ
SiO_2	SiO_2	Ca	5-10	>10
Fe_2O_3	$CaSO_4$	S	5-10	>10
$CaSO_4$	CaS	O	5-10	>10
CaS	Fe_2O_3	Si	>10	>10
CaO		Fe	1-5	5-10
		K	5-10	5-10
		Al		1-5
		Mg		1-5
		Cl		1-5
		Ti		1-5

Elements and compounds not detected in flue gas particulates

Be
MgF
$MgCO_3$
CaF_2
SrF_2
Ba^{+2}
Tl
P
PO^{-3}
TiO^3
FeO^2
Ru
Co^{+2}
Co^{+3}
Rh
Ni^{+2}
Ni^{+3}
Th
U
Rb
Ca

KEY: IR = Infrared

ESCA = Electron Spectroscopy for Chemical Analysis

XRD = X-ray Diffraction

EMPA = Electron Beam Microprobe Analysis

TABLE 11. POLYCYCLIC ORGANIC MATERIAL ANALYSIS
(Values in ng/g or ng/m^3 where appropriate)

	Particulates						Flue gas		
	Cyclone 2 or coarse dust			Small particles					
	Battelle[a]	Leatherhead[b]	Exxon	Battelle[a] <27µ	Exxon <3µ	Leatherhead[b] exhaust dust	Battelle[a]	Exxon[c]	Leatherhead
Anthracene/phenanthrene	<0.24	0.13	<0.3-4	429.3	<0.3-14	*	2667-57300	53	93
Benzo(b)fluoranthene		*		31.2		*	8.8	1.0	*
Benzo(a)pyrene		*				*		0.5	*
Benzo(e)pyrene		*		19.5		*	3.5		*
Benzo(g,h,i)perylene		*		3.9		*	3.5		*
Benzo(c) Phenanthrene		*		9.8		*	14-170	0.2	3
Chrysene/benz(a)anthrancene		*		39		*	35.1-370	3.8	3
Coronene		*					*		*
Dibenzo(a,h)anthracene		*		*		*	*		*
Dibenzo(a,h)carbazole		*							*
Dibenzo(c,g)carbazole				*			*		
Dibenzo(ai & ah)pyrenes		*		*		*	*		*
7,12-Dimethylbenz(a)anthracene		*		*		*	*		*
Fluoranthene		*	<0.3-0.4	175.4	<0.3-2	*	1404-3200	26	21
Indeno(1,2,3,cd)pyrene		*		3.9		*	3.5		*
Methyl anthracenes		*	<0.2	39.0	<0.2	*	561-9400	5	10
Methyl benzopyrene		*		3.9		*	1.8		*
3-Methyl cholanthrene		*		*		*	*		*
Methyl chrysenes		*		5.8		*	3.5-170		<0.7
Methyl pyrene/fluoranthene		*		7.8		*	28.1-730	1.0	7
Perylene		*		*		*	*		*
Pyrene		*	<0.2				211-950	9	9
*value less than		0.1		0.7		0.2	0.4		0.1

[a] Merryman et al., 1977.

[b] Pillai and Roberts, 1977.

[c] Murthy and Henschel, 1978.

Two other carcinogens, dimethyl and monomethyl sulfate, have been found in the ambient air around a power plant burning low-sulfur, high-ash coal (Eatough, 1979). The methylated sulfate concentrations may be as high as 1,000 ppm on respirable particles less than one micron, with an atmospheric residence time of hours or days. The decomposition point of dimethyl sulfate is 188°C which means the material must be formed downstream of the combustion chamber. The material could be formed in the following reaction:

$$5CO + SO_2 + 3H_2O \rightleftharpoons (CH_3O)_2SO_2 + 3CO_2 \qquad (15)$$

This finding must be further examined.

Dow Chemical Company has also reported the presence of dioxins in combustion products from fireplaces, refuse incinerators, automobiles, trucks, charcoal grilles, cigarettes and fossil-fueled power plants. Based on this, the EPA is initiating a testing program covering all emission sources, stack, fly ash and wastewater streams in incinerators and power plants to verify the findings and to determine if regulatory activity is warranted (Environment Reporter, 1979). This finding must also be checked for FBC units.

Actual test data on FBC effluents obtained from bench scale, pilot plant, and demonstration scale processes shows that pollutant concentrations vary. As shown in Tables 12 and 13, investigation has focused on flue gas and spent bed and ash reject material. Caution and restraint must be used in extrapolating this experimental data to commercial-size FBC units.

The types and quantities of pollutants formed and discharged from FBC processes depend on many FBC system variables:

- Combustion temperature
- Combustion pressure
- Fluidized bed height and freeboard in combustion chamber
- Type of coal(impurities)
- Fuel feed rate
- Air flow rate
- Sorbent feed rate
- Superficial velocity
- Ca/S mole ratio
- Sorbent and fuel particle size
- Pollution control equipment
- Mode of operation
- Fugitive releases during process breakdowns

TABLE 12. INORGANIC ANALYSIS OF PARTICULATE EMISSIONS IN FLUE GAS (Murthy et al., 1977)

	Size range	
Substance	1-3 (microns)	3-10 (microns)
	Major elements, μg/g	
Al	200,000	200,000
Fe	60,000	20,000
Si	200,000	200,000
K	3,000	1,500
Ca	30,000	30,000
C (Total carbon)	12,000	11,000
	Anions, weight percent	
Cl^-	0.011	0.007
F^-	0.031	0.032
$Co_3^=$	<0.2	<0.2
$SO_3^=$	0.001	0.004
S=	<0.03	0.03
NO_3^-	<0.001	<0.001
NO_2^-	<0.001	<0.001

A major group of pollutants, fugitive emissions, are site-specific and do not lend themselves to generic treatment. These pollutants originate from vents, loose system components (seals, connections, valves, etc.), careless materials handling, coal and sorbent storage piles, and other sources. Airborne fugitive emissions associated with coal-fired operations commonly originate from piles of stored coal, combustion residues from furnace cleaning, and collected particulate matter from air pollution control equipment. The piles of material are stored outside and are subject to wind action. Water-borne fugitive emissions usually originate by leaching of feed and residue storage piles, subsurface disposal, surface runoff, and atmospheric washout of combustion products not controlled at the site.

The significance of fugitive emissions, in the context of all other emissions from FBC operations, is relatively undefined. They are usually caused by careless and poorly maintained operations. Proper materials handling, enclosed short-term storage of feed stock and residues, and good housekeeping can probably eliminate any significant fugitive emissions.

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TABLE 13. TRACE METALS IN BED REJECT MATERIAL
(Murthy et al., 1977)

Element	Observation (μg/g and Percent)	Element	Observation (μg/g and Percent)
Li	200	Ag	<0.1
Be	0.3	Cd	<0.5
B	30	In	<0.6
F	0.3	Sn	2
Na	300	Sb	1
Mg	20%	Te	<0.4
Al	1.5%	I	<0.07
Si	1.5%	Cs	4
P	50	Ba	30
S	1.5%	La	7
Cl	40	Ce	7
K	1%	Pr	1
Ca	20%	Nd	1.5
Sc	3	Sm	0.5
Ti	200	Eu	3
V	20	Gd	1
Cr	30	Tb	0.3
Mn	100	Dy	<0.1
Fe	1%	Ho	<0.3
Co	1.5%	Er	<0.1
Ni	150	Tm	<0.3
Cu	15	Yb	<0.3
Zn	400	Lu	<0.3
Ga	7	Hf	<0.4
Ge	40	Ta	<0.4
As	20	W	<0.4
Se	3	Re	<0.4
Br	3	Os	<0.2
Rb	60	Ir	<0.4
Sr	300	Pt	<0.1
Y	1.5	Au	<0.4
Zr	0.5	Hg	<0.2
Nb	2	Tl	2
Mo	2	Pb	<0.15
Ru	<1	Bi	0.2
Rh	<0.5	Tn	0.4
Pd		U	

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The fugitive emissions generated during process breakdown or during malfunction of pollution control equipment can be readily predicted by estimating what untreated waste streams produce. Generally only treated waste discharges are monitored, but sufficient data are available on the efficiency of contaminant-removal of pollution control equipment so that raw emissions can be back-calculated. Fugitive emission rates then can be estimated with relatively close accuracy.

Solid Wastes and Leachates

As currently envisioned, the use of FBC for industrial and utility applications will utilize a once-through-and-discard cycle with respect to the material used as a sulfur acceptor (probably limestone or dolomite). The basic FBC unit produces no aqueous discharges; however, disposal of the spent bed material is likely to result in leachate which could contaminate surface or groundwater systems if improperly disposed. For FBC to be functional, additional processes such as heat transfer systems or electric power generators are required.

Heat transfer systems and electric generating systems, however, are potential sources of water pollutants. The pollutants are derived from the system blowdown and water treatment chemicals used. Another source of potential pollutants common to all facilities using coal is leachate formed by dissolution of soluble species in coal by rainwater and melting snow. In addition to coal pile leachate, FBC operations could generate leachate from stored limestone or other sulfur acceptor material.

Figure 7 is a simplified materials flow illustration, indicating potential sources of aqueous pollutants. Depending on the materials handling and storage procedures at various plants, the amounts and type of pollutants discharged may vary considerably. All plants are expected to utilize coal as the primary fuel and either limestone or dolomite as the sulfur absorbent. The coal and sorbent may be stored in the open or in enclosed silos, as is done at the 30 MW units at Georgetown and Rivesville. Large, utility-size units would be expected to store both coal and limestone in the open primarily because of the quantities that must be kept on hand. Typically, a coal-fired utility plant would maintain a 75 to 90-day coal supply (Federal Power Commission, 1974a) which amounts to 810 tons per megawatt.

Whenever coal is stored exposed to the weather, drainage will occur. Coal pile drainage is typically acidic, high in suspended and dissolved solids, high in iron, sulfur, manganese and hardness. Ranges of concentration of pollutants from coal piles from two studies are summarized in Table 14. The amount and quality of the leachate depend on several factors, such as amount of precipitation, duration, intensity, etc.; turnaround time of piles; and quality of coal.

Sorbent Leachate

Leachate from exposed limestone or dolomite piles will have a pH generally in excess of nine, and be high in suspended solids. Sodium may also be present in significant amounts (Stone and Kahle, 1977). Like the coal pile leachates, the quality of sorbent leachates will vary with the amount of water and with time of contact of water and sorbent.

Boiler Blowdown

Chemical additives are used to prevent corrosion, control pH and scale formation, and prevent solids deposition in steam generators, heat transfer lines, and boilers. The chemical additives used are summarized in Table 15. Factors which determine the quality of boiler water blowdown include:

- Boiler design pressure
- Chemicals used in water treatment
- Quality of water used in boiler

In addition to the chemicals used in water treatment, boiler blowdown commonly contains calcium and magnesium scale, iron and copper oxides, and sometimes elemental copper.

Cooling System Effluents

Two types of cooling systems are in common use, once through cooling systems and recirculating cooling systems. For the former, the primary pollutant is waste heat. The chemical composition of the effluent is essentially the same as the influent water; the solids may be slightly higher due to evaporation, introduction of corrosion products, and use of biocides. Commonly used biocides include chlorine and sodium or calcium hypochlorite. Cooling water is generally chlorinated by shock methods wherein large doses are added intermittently.

Recirculating cooling systems may utilize cooling towers, ponds, or canals to collect cooling water, dissipate heat and allow re-use of the water. Since evaporation is the major cooling mechanism, water vapor is a major atmospheric discharge. Along with the water vapor, small amounts of organic and inorganic water contaminants and chemicals used in water treatment may become airborne in the form of aerosols.

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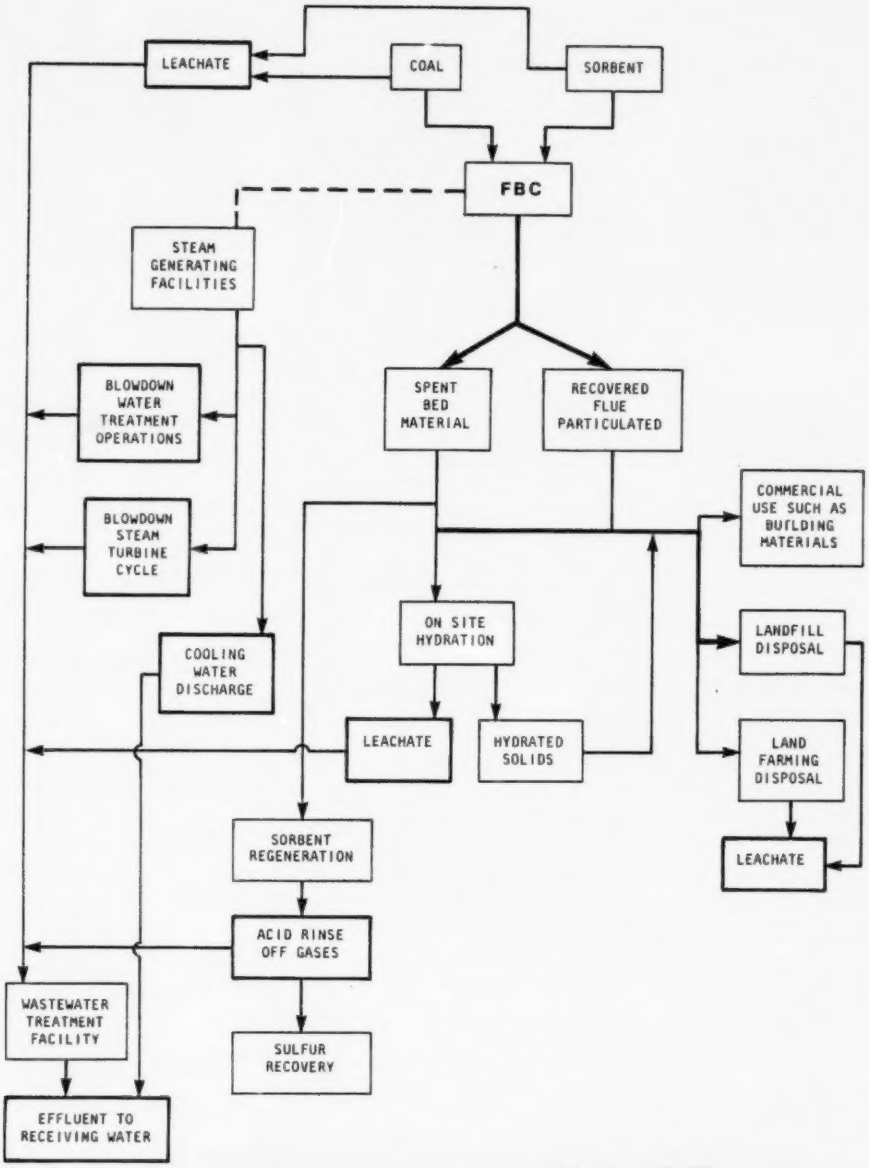
LEACHATE
COAL
SORBENT
FBC
STEAM GENERATING FACILITIES
BLOWDOWN WATER TREATMENT OPERATIONS
BLOWDOWN STEAM TURBINE CYCLE
COOLING WATER DISCHARGE
SPENT BED MATERIAL
RECOVERED FLUE PARTICULATED
COMMERCIAL USE SUCH AS BUILDING MATERIALS
ON SITE HYDRATION
LANDFILL DISPOSAL
LEACHATE
HYDRATED SOLIDS
LAND FARMING DISPOSAL
LEACHATE
SORBENT REGENERATION
ACID RINSE OFF GASES
WASTEWATER TREATMENT FACILITY
SULFUR RECOVERY
EFFLUENT TO RECEIVING WATER

Figure 7. Scheme of FBC (materials flow).

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TABLE 14. POLLUTANTS FROM LEACHING OF COAL PILES[a]

Pollutant	Concentration[b]	Concentration[c]
Phosphorus		0.2-1.2
Ammonia		0-1.8
Nitrate		0.3-2.3
Alkalinity		15-80
BOD		3-10
COD		85-1100
pH	2.3-3.1	2.1-7.8
Acidity	300-7100	10-22,000
Conductivity	2400-6400	
Chloride	0-660	4-480
Sulfate	1800-96,000	130-19000
Dissolved Solids	270-16,000	250-29,000
Suspended Solids	8-2300	20-3300
Iron	23-1800	0.17-4700
Manganese	1.8-45	
Silica	1-390	
Copper	0.07-1.4	1.6-1.8
Zinc	1.1-16.6	0.001-12.5
Chromium	<0.005-0.011	0-15.7
Aluminum	20-440	
Nickel	0.15-4.5	
Calcium	31-720	
Magnesium	17-480	
Lead	<0.01	
Mercury	<0.0002-0.0072	
Barium	<0.1-0.5	
Arsenic	0.006-0.36	
Cadmium	<0.001-0.003	
Selenium	<0.001-0.030	
Titanium	<1.0	
Beryllium	<0.01-0.07	
Antimony	<0.1-1.8	

[a] All measurements in mg/ℓ except conductivity (μmhos/cm) and pH.

[b] Cox et al., 1979.

[c] Nichols, 1974.

TABLE 15. CHEMICAL AGENTS ASSOCIATED WITH BOILER TREATMENT
(Sugarek and Sipes, 1978)

Control objective	Candidate chemical additives	Residual concentration in boiler water
Scale	Di- and tri-sodium phosphates	3-60 mg/ℓ as PO_4
	Ethylene diaminetetracetic acid (EDTA)	20-100 mg/ℓ
	Nitrilotriacetic acid (NTA)	10-60 mg/ℓ
	Alginates	up to 50-100 mg/ℓ
	Polyacrylates	up to 50-100 mg/ℓ
	Polymethacrylates	up to 50-100 mg/ℓ
Corrosion	Sodium sulfite and catalyzed sodium sulfite	less than 200 mg/ℓ
	Hydrazine	5-45 mg/ℓ
	Morpholine	5-45 mg/ℓ
pH	Sodium hydroxide	Added to adjust boiler water ph to the desired level, typically 8.0 - 11.0.
	Sodium carbonate	
	Ammonia	
	Morpholine	
	Hydrazine	
Solids Deposition	Starch	20-50 mg/ℓ
	Alginates	20-50 mg/ℓ
	Polyacrylamides	20-50 mg/ℓ
	Polyacrylates	20-50 mg/ℓ
	Polymethacrylates	20-50 mg/ℓ
	Tannins	≤200 mg/ℓ
	Lignin derivatives	≤200 mg/ℓ

Chemicals are added to recirculative cooling systems to prevent or control corrosion, pH, and biological growth. Because of evaporation, the treatment chemicals and contaminants native to the water used are concentrated. These pollutants are periodically removed in the blowdown, at a rate ranging from 0.5 to 3 percent of the recirculating water flow (Donahue, 1970). Some of the major chemicals used for water treatment in recirculating cooling systems are summarized in Tables 16 and 17.

Additional potential pollutants created in the system may result when chlorine, added to prevent biological growth, reacts with hydrocarbon contaminants in the water and forms undesirable chlorinated hydrocarbons. Another source of water contaminants may be contact of the water with the atmosphere; in some cases, 80 percent of the suspended solids in the cooling water has been attributed to atmospheric contaminants. Soluble gases may also contaminate the cooling water.

Sorbent Regeneration

When the process of sorbent regeneration is commercialized, it may produce some water pollutants. The process is essentially a dry process; however, the off gas containing concentrated levels of sulfur dioxide may require an acid rinse prior to reduction to sulfur. Sulfuric acid would be the expected rinsing acid. Ultimately, the acid would become contaminated and require renewal. The acid discharge would be expected to be highly contaminated with both inorganic and organic species and with suspended solids.

In addition to the specific process effluents, other sources of water pollutants which may be derived from operation of an FBC power generating or energy conversion plant include:

- Equipment cleaning
- General plant discharge
- Process spills and leaks
- Miscellaneous sources such as laboratory or machine shop wastes

All of these sources, individually or in combination, may create potentially toxic or hazardous aqueous pollutants. The wastes from the various processes may be treated on site and the effluent discharged to a sewer or surface water, or the wastes may be directly discharged to a sewer system. If treated on-site, these aqueous waste streams would most likely be combined. Since some of the wastewater streams are acidic, and others basic, the combined wastewater will be at least partially neutralized. Removal of organic and inorganic

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TABLE 16. CHEMICALS USED IN RECIRCULATIVE COOLING WATER SYSTEMS (Federal Power Commission, 1974b)

Use	Chemical
Corrosion inhibition or scale prevention in cooling towers	Organic phosphates Sodium phosphate Chromates Zinc salts Synthetic organics
Biocides in cooling towers	Chlorine Hydrochlorous acid Sodium hypochlorite Calcium hypochlorite Organic chromates Organic zinc compounds Chlorophenates Thiocyanates Organic sulfur compounds
pH control in cooling towers	Sulfuric acid Hydrochloric acid
Dispersing agents in cooling towers	Lignins Tannins Polyacrylonitrile Polyacrylamide Polyacrylic acids Polyacrylic acid salts
Biocides in condenser cooling water systems	Chlorine Hypochlorites Sodium pentachlorophenate

TABLE 17. COOLING TOWER CORROSION AND SCALE INHIBITOR SYSTEMS (Suprenant et al., 1976)

Inhibitor system	Concentration of chemical additives in recirculating water
Chromate	200 - 500 mg/ℓ CrO_4
Chromate + Zinc	17 - 65 mg/ℓ CrO_4
	8 - 35 mg/ℓ Zn^{++}
Chromate + Zinc + Phosphate (inorganic)	10 - 15 mg/ℓ CrO_4
	8 - 35 mg/ℓ Zn^{++}
	30 - 45 mg/ℓ PO_4
Zinc + Phosphate (inorganic)	8 - 35 mg/ℓ Zn^{++}
	15 - 60 mg/ℓ PO_4
Phosphate (inorganic)	15 - 60 mg/ℓ PO_4
Phosphate (organic)	15 - 60 mg/ℓ PO_4
	3 - 10 mg/ℓ organics
Organic Biocide	30 mg/ℓ chlorophenol
	5 mg/ℓ sulfone
	1 mg/ℓ thiocyanate

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species from the wastewater streams may require some form of flocculation, precipitation, and sedimentation. Possible treatment chemicals may include soda-lime combination or spent bed material. The effluents from the wastewater treatment process and the resultant sludge may include as contaminants any of the chemicals or elements listed in Tables 16 and 17.

The accumulated sludge and other solid wastes may be transferred to landfills for ultimate disposal. The solid wastes which may require disposal include:

- Spent bed materials composed primarily of calcium and/or magnesium carbonates, sulfates and oxides
- Particulate matter from cyclones or baghouses
- Particulates, spent bed material or bottom ash from carbon burnup

If the plant is sufficiently large that regeneration of sorbent is economically practicable, the only major sources of solid wastes requiring disposal would be the particulates captured by cyclones, baghouses, or other techniques. A similar situation would occur if the spent bed material were transported to another facility which specialized in sorbent regeneration and sulfur recovery.

Whether the spent bed material and the captured flue particulates, as well as wastewater treatment sludge, are individually disposed or combined for ultimate disposal, the major environmental contaminants will result from leachate formation. The leachate formed within a landfill may contaminate surface water and/or groundwater. Groundwater may feed surface waters and vice versa, resulting in cross-contamination. Representative concentrations of elements in spent bed material leachate are summarized in Table 18. The leachate data for the Exxon Miniplant is taken as the highest concentrations measured on several samples by two methods of producing leachate. The values presented for the Level 2 analysis are the sum of acidic and basic leachate concentrations.

Table 19 summarizes leachate data obtained from flue gas particulates. The data from the Exxon plant represent data obtained from leaching of particulates captured by the second of two cyclones installed in the exhaust gas line. The data from the Level 2 analysis represent leachate from captured flue gas particulates greater than 27 microns.

Table 20 presents data on leachate from Pressurized and Atmospheric FBC unit solid wastes. These analyses, performed by the Westinghouse Research and Development Center (Sun and

TABLE 18. REPRESENTATIVE CONCENTRATIONS OF ELEMENTS IN LEACHATE OF FBC SPENT BED MATERIAL[a]

Element	Exxon[b]	Level[c]	Element	Exxon[b]	Level[c]
Lithium	1,000	580	Arsenic	150	N.D.
Beryllium	1.5	N.D.	Selenium	100	N.D.
Boron	300	31,000	Bromine	300	N.D.
Fluorine	6	N.D.	Rubidium	300	N.D.
Sodium	15,000	17,000	Strontium	700	390
Magnesium	20,000	1,400	Ytterium	7	N.D.
Aluminum	3,000	7,400	Zirconium	30	N.D.
Silicon	25,000	260,000	Molybdenum	400	60
Phosphorus	3,000	N.D.	Rhodium	< 1	N.D.
Sulfur	1,500,000	N.D.	Silver	10	4
Chlorine	2,000	N.D.	Cadmium	< 2	N.D.
Potassium	15,000	7,200	Mercury	< 2	<N.D.
Calcium	1,000,000	1,300,000	Thallium	< 2	N.D.
Scandium	< 2	N.D.	Lead	20	230
Titanium	1,000	N.D.	Tin	100	N.D.
Vanadium	100	< 20	Antimony	1	N.D.
Chromium	200	N.D.	Tellurium	6	N.D.
Manganese	30	N.D.	Iodine	7	N.D.
Iron	3,000	800	Cesium	20	N.D.
Cobalt	5	N.D.	Barium	700	N.D.
Nickel	500	170	Lanthanum	70	N.D.
Copper	150	14	Cerium	1	N.D.
Zinc	<40	220	Neodymium	4	N.D.
Gallium	5	N.D.	Tungston	20	N.D.

[a] Concentrations in μg/ℓ; N.D. = not detected.

[b] Allen et al., 1977.

[c] Ryan et al., 1979.

TABLE 19. LEACHATES FROM FLUE GAS PARTICULATES COLLECTED FROM FBC PROCESSES[a]

Element	Exxon[b]	Level 2[c]	Element	Exxon[b]	Level 2[c]
Lithium	2,500	70	Arsenic	70	300
Beryllium	0.2	20	Selenium	200	N.D.
Boron	600	25,000	Bromine	15	
Fluorine	15	N.D.	Rubidium	500	N.D.
Sodium	15,000	126,000	Strontium	4,000	830
Magnesium	100,000	5,600	Ytterium	2	N.D.
Aluminum	15,000	16,500	Zirconium	25	7
Silicon	15,000	300,000	Molybdenum	100	170
Phosphorus	700	N.D.	Rhodium	N.D.	N.D.
Sulfur	2,000,000		Silver	2	N.D.
Chlorine	2,000		Cadmium	N.D.	N.D.
Potassium	150,000	22,000	Mercury	N.D.	N.D.
Calcium	700,000	310,000	Thallium	N.D.	N.D.
Scandium	3	N.D.	Lead	20	100
Titanium	500	N.D.	Tin	7	N.D.
Vanadium	250	50	Antimony	2.5	N.D.
Chromium	150	N.D.	Tellurium	2	N.D.
Manganese	15	1,400	Iodine	15	N.D.
Iron	2,500	23,000	Cesium	20	N.D.
Cobalt	N.D.	N.D.	Barium	2,000	N.D.
Nickel	150	N.D.	Langhanum	10	N.D.
Copper	70	16	Cerium	5	N.D.
Zinc	N.D.	N.D.	Niodymium	4	N.D.
Gallium	20	N.D.	Tungsten	10	N.D.

[a] Concentrations in μg/ℓ; N.D. = not detected.

[b] Allen et al., 1978.

[c] Ryan et al., 1979.

McAdams, 1979), compare FBC solid waste leachate data to regulations being promulgated under the Resource Conservation and Recovery Act (RCRA). The leachate tests were performed in accordance with the RCRA procedure. The material tested included spent bed material, carryover (solids captured by the second cyclone), and fines (solids captured by a third cyclone, baghouse, or other filter). Pertinent anion data from some leachate studies on FBC solid wastes are summarized in Table 21.

Biological Examination

Comprehensive biological examination of the waste streams from FBC plants is just beginning. The fine particulate stream from the Exxon miniplant had a positive Ames Test and showed cytotoxicity with rabbit alveolar macrophages. Leachate from the second cyclone catch exhibited toxicity to saltwater organisms, and, along with bed reject material leachate, exhibited toxicity to freshwater organisms (Murthy and Henschel, 1978). In a preliminary examination, the fine particulate matter from the Argonne combuster also showed a positive Ames Test but only under startup conditions. At steady state conditions, the fine particulate catch appeared to be non-mutagenic (Norris, B., Argonne National Laboratory, to Blair, T., personal communication). Argonne researchers are also exposing mice to a diluted exhaust gas stream. The preliminary results indicate low immediate toxicity which might correlate with the negative results on the plant ethylene stress test for the Exxon unit. Further examination is in order and caution is warranted in waste disposal.

POLLUTION CONTROL

Background

One of the major advantages of FBC over conventional pulverized coal combustion processes is that it burns high-sulfur coal and control emissions of SO_2 and NO_x in the combustion chamber. As stated previously, the limestone is calcinated to produce lime (CaO) in the fluidized bed at temperatures of 750 to 950°C.(1,400° to 1,800°F). The combustion of coal releases the sulfur in the bed in the form of sulfur dioxide (SO_2) which reacts with lime (CaO) to produce calcium sulfate ($CaSO_4$). The calcium/sulfur molar feed ratio is about 3:1 for limestone ($CaCO_3$) and reduces SO_2 emissions by over 90 percent. For dolomite ($MgCa[CO_3]_2$) the ratio is 2:1. The sulfur extraction is sufficiently high to reduce the SO_2 emissions to meet the air quality standards for coal-fired boilers. Because of lower combustion temperatures in the fluidized bed, NO_x gas formation is suppressed below the level requiring additional pollution control systems.

TABLE 20. POM COMPOUNDS IN LEACHATES FROM AFBC AND PFBC COMBUSTION OF COAL SOLID WASTES

	Leatherhead[a] µg/kg in solid waste			
Component	Bed reject material	Primary cyclone	Secondary cyclone	Exhaust dust
Anthracene/Phenanthrene	<0.1	0.1	0.13	<0.2
Methylanthracenes	<0.1	3	<0.1	<0.2
Fluoranthene	<0.1	<0.1	<0.1	<0.2
Pyrene	<0.1	<0.1	<0.1	<0.2
Methylpyrene/Fluoranthene	2.4	<0.1	<0.1	<0.2
Benzo(c)phenanthrene	<0.1	<0.1	<0.1	<0.2
Chrysene/Benz(a)anthracene	<0.1	<0.1	<0.1	<0.2
Methylchrysenes	<0.1	<0.1	<0.1	<0.2
7,12-dimethylbenz(a)Anthracene	<0.1	<0.1	<0.1	<0.2
Benzo fluoranthenes	<0.1	<0.1	<0.1	<0.2
Benz(a)pyrene	<0.1	<0.1	<0.1	<0.2
Benz(e)pyrene	<0.1	<0.1	<0.1	<0.2
Perylene	<0.1	<0.1	<0.1	<0.2
Methylbenzopyrenes	<0.1	<0.1	<0.1	<0.2
3-Methylcholanthrene	<0.1	<0.1	<0.1	<0.2
Indeno(1,2,3-cd)pyrene	<0.1	<0.1	<0.1	<0.2
Benzo(ghi)perylene	<0.1	<0.1	<0.1	<0.2
Dibenzo(a,h)anthracene	<0.1	<0.1	<0.1	<0.2
Dibenzo(a,h)carbazole	<0.1	<0.1	<0.1	<0.2
Dibenzo(ai & ah)pyrenes	<0.1	<0.1	<0.1	<0.2
Coronene	<0.1	<0.1	<0.1	<0.2

[a] Pillai and Roberts, 1977.

TABLE 21. ANION ANALYSIS OF LEACHATE OF FBC SOLID WASTES (Allen et al., 1977)

	anion - µg/l					
Wastes	Cl	F	SO_4	SO_3	NO_3	NO_2
Bed Reject Material	176,000	4,000	3,000,000	3,100	8,300	1,900
Cyclone #2 Dust	65,000	2,400	2,500,000	2,300	6,700	71,000

Basic problems--extent of particulate control, toxic trace elements, and gaseous organic pollutants--are still relatively undefined. However, experimental evidence (Murthy et al., 1977), shows that particulates, certain trace elements, and certain gaseous organic compounds are emitted in sufficiently high concentrations in the flue gas to warrant installation of pollution control equipment. Experimental data and theoretical considerations indicate that conventional pollution control equipment used on coal-fired systems will be applicable to FBC operations, with a similar level of control. The basic classes of applicable air pollution control equipment are:

- Cyclones (single and multiple stage)
- Fabric and granular bed filters
- Catalytic and thermal oxidizers
- Electric precipitators (single and multiple stage--high volt and low volt)
- Scrubbers

Combinations of these categories of equipment can be designed into pollution control systems that would allow FBC of coal processes to meet the New Source Performance Standards (NSPS).

The solid wastes and possible secondary water contaminants present a set of different problems and need to be considered in detail within the context of a total waste management system for coal combustion and conversion processes.

Discharges from atmospheric and pressurized FBC processes are emitted under different conditions (i.e., temperature, pressure) and therefore may require different pollution control system design. However, the general categories of pollution control equipment will be applicable to both Atmospheric FBC and Pressurized FBC processes.

Applicability of different pollution control equipment depends on the physical size and reactivity of the individual contaminant particles. Figures 8 and 9 show the relationship of contaminant particle size and the types of pollution control equipment applicable.

One form of pollution control that must not be overlooked is coal pretreatment and fractionation. For example, density fractionation of coal from the Upper Freeport Coalbed, Garett County, Maryland, indicates that removal of the sink 1.60 fraction would reduce the mercury concentration by 47 percent, sulfur 42 percent, chromium 29 percent, copper 43 percent, nickel 28 percent and manganese 50 percent. Other coals, of course, show different removal patterns. Cadmium in the coal

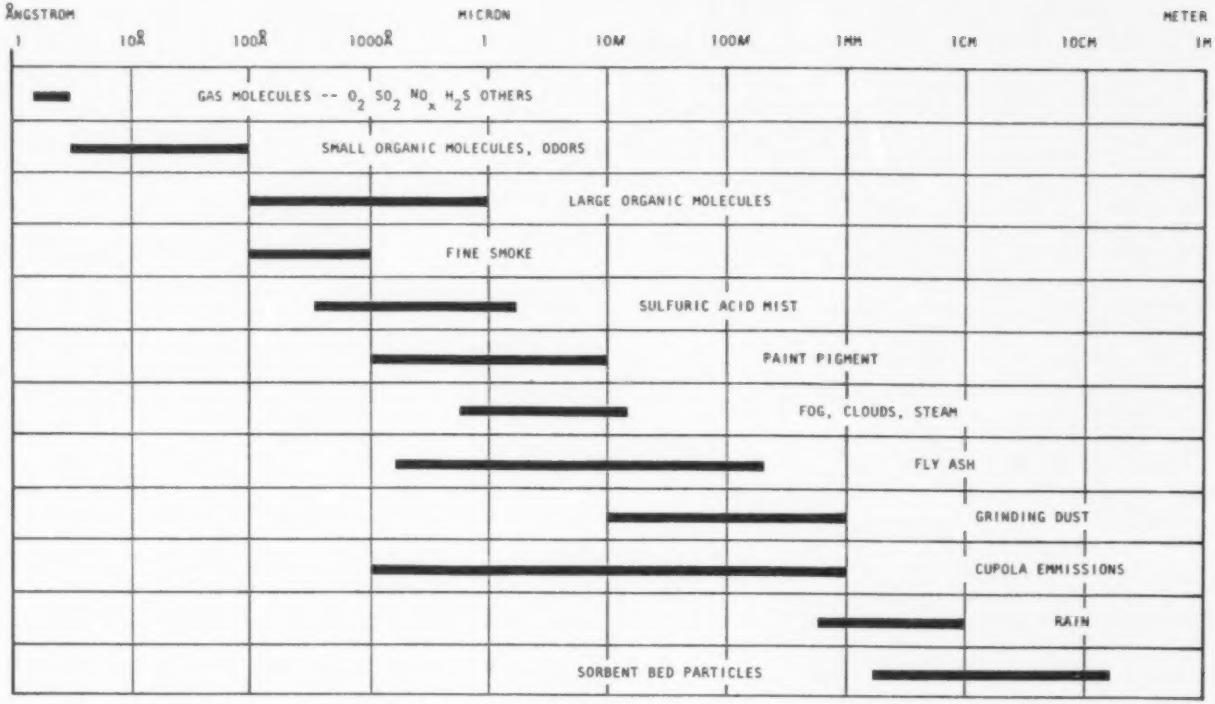


Figure 8. Air pollutant particle sizes.

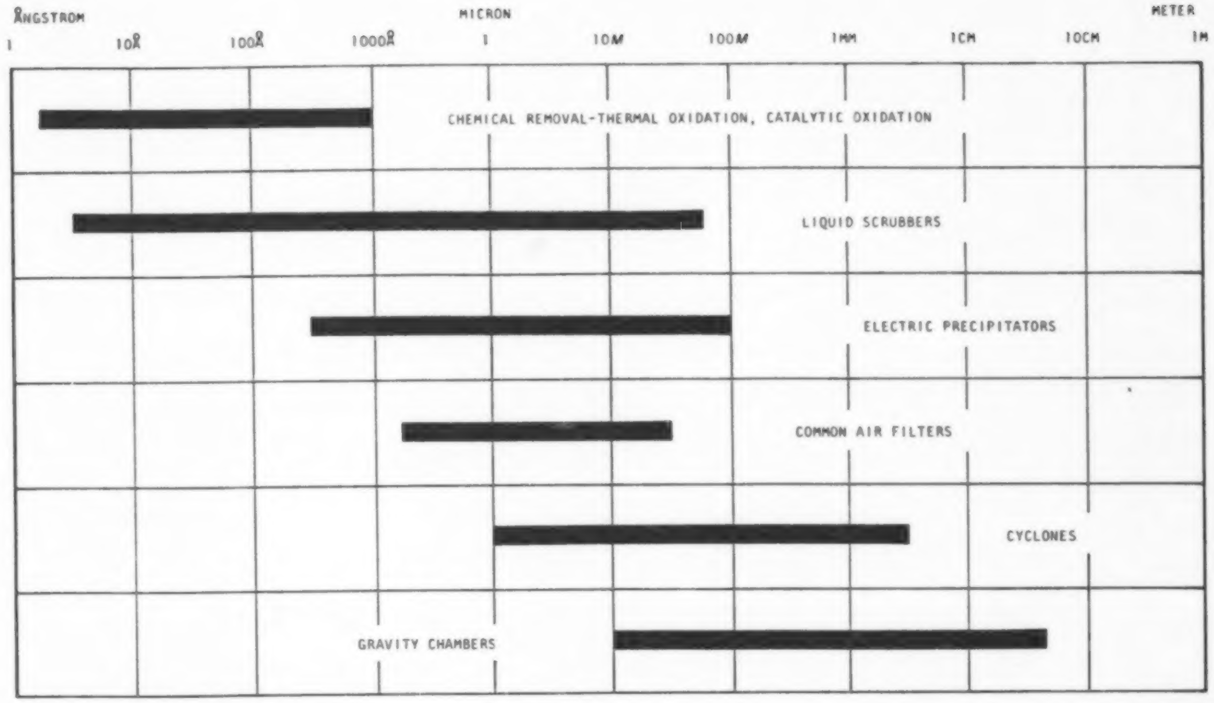


Figure 9. Emission control equipment chart.

from Hazard No. 4 Coalbed, Bell County, Kentucky, is evenly distributed throughout the various density fractions (Schultz et al., 1975). The cadmium is probably attached to the carbonaceous material rather than associated with the pyritic material as are the other elements. The economics of limestone mining, calcination, and spent bed material disposal versus the amount of removable sulfur will be the major determining factor for coal pretreatment.

Pollution Control of Flue Gases

General Pollution Control Applications--

Theoretical calculations (Fennelly et al., 1977) and experimental data (Murthy et al., 1977) show that the major gaseous contaminants from FBC process flue gas occur in relatively manageable concentrations and emission rates. Conventional commercially available air pollution control devices and systems can reduce the contaminant emissions from FBC processes to meet air pollution standards.

Particulate matter emitted by FBC processes can also be readily removed by commercially available cyclones and electric precipitators with sufficiently high efficiencies to comply with current air quality standards. Although a fraction of particulates from FBC processes will be generated from the fluidized bed media, the sorbent (limestone and/or dolomite) and the general nature of the particulate handling systems will be nearly the same as for the conventional coal-fired boilers, except that the highly reactive CaO particles may have to be stabilized before or during collection. This similarity will probably place the FBC processes under the same air quality compliance requirements. The contaminant removal efficiency of each category of equipment varies greatly with the conditions of FBC operation and the commercial design of the pollution control equipment. The range of contaminant removal efficiency of the general types of equipment is given in Table 22.

A major concern in the pollution control process is to remove particulates that are less than 3 microns. These particulates are of much concern because they are less efficiently captured by the particulate control devices, have a long atmospheric residence time, are deposited efficiently in the deep lung and only slowly removed, and because the smallest particles concentrate the most toxic elements. In the lung, serum can solubilize up to 80 percent of the trace elements on the particle versus at most 15 percent in the stomach (Piperno, 1975). Polycyclic organic matter can be deposited on the particles depending upon the temperature at which the particulate collection occurred. In one study, an electrostatic precipitator operating above 100°C collected

TABLE 22. MAJOR CONTAMINANTS IN THE FLUE GAS OF FLUIDIZED BED COMBUSTION OF COAL AND APPLICABLE POLLUTION CONTROL EQUIPMENT

Contaminants	Effective and applicable pollution control systems				
	Filters[a]	Scrubbers[b]	Thermal or[c] catalytic oxidation	Electric[d] precipitators	Cyclones[e]
CO			X		
HC	X		X		
H_2SO_4(mist) + SO_3	X	X			
SO_2	X	X			
NH_3		X			
CN		X			
Cl		X			
NO_x			X		
Particulates 100 to 1000 microns	x	x			x
Particulates 10 to 100 microns	x	x			x
Particulates 1 to 10 microns	x	x		x	
Particulates 1 micron	x	x		x	
Trace elements and compounds[f]	x	x	x	x	x

[a] Filter efficiency and applicability greatly depends on the filter media - fabric type, granular, etc. Gravel bed filters can be used for sulfur removal.

[b] Scrubber efficiency and applicability is dependent primarily on the scrubbing liquid used and the pressure drop.

[c] The need for thermal and catalytic oxidation can be eliminated for CO and HC_x by increasing combustion efficiency in the burner.

[d] Electric precipitators can be low volt, high volt, single and multiple stage, depending on the efficiency desired.

[e] Cyclones remove most particulate matter 100 to 1000 microns.

[f] Trace elements will be removed in fractions by any of these systems in conjunction with other contaminants.

large and small particles, with no mutagenic activity; yet, at 95°C, stack samplers after the precipitator collected mutagenic particulates (Fisher et al., 1979). The presence of particulates along with the PAH material exacerbates the carcinogen problems in that the fine solids can cause damage by themselves or they can act as a cocarcinogen in the two-stage carcinogenesis model (National Academy of Sciences, 1972). Also, the fine particulates can combine with SO_2 to form a toxic, hazardous material in the atmosphere.

Carbon Utilization--

Efficient carbon utilization is important in reducing potentially toxic carbon compounds, maintaining thermal efficiency, and in reducing capital and operating costs. The carbon efficiency of a coal combustor/boiler can be defined as:

$$C_u = \frac{\text{Carbon in Coal - Carbon Lost}}{\text{Carbon in Coal}} \times 100 \qquad (16)$$

For FBC units, efficiencies near 100 percent can be obtained only if the large particle fly ash trapped in the particulate removal systems is recombusted. This requires either a carbon burn-up cell operating at high temperatures (1,100°C [2,000°F]), or that the fly ash be reinjected into the fluid bed. Typical combustor carbon losses are shown in Table 23 for a PFBC. Particulate reinjection into the bed is relatively simple for an AFBC unit, but a combustor such as the multi-solid FBC variant requires more sophisticated recycling to achieve high carbon utilization efficiencies (Liu et al., 1979).

TABLE 23. DISTRIBUTION OF COMBUSTIBLE LOSSES
(Hoy and Roberts, 1977)

Source	Typical range %
Carbon monoxide	0.04 - 0.10
Carbon content of	
(a) bed material	0.05 - 0.20
(b) 1° cyclone dust	1.00 - 5.00
(c) 2° cyclone dust	<0.01 - 4.00

Hydrocarbons (HC_x) and carbon monoxide (CO) emissions can be significantly reduced by maintaining high oxygen concentrations, as shown in Figure 10. Also, low superficial velocities help reduce emissions. The conventional pulverized coal combustion units produce very low HC concentrations in the stack gases (Merryman et al., 1977). The Babcock and Wilcox experimental AFBC unit is monitored for CO with automatic coal feed shutoffs when CO concentrations in the flue gas exceed 0.1 percent (GCA/Technology Division, 1978).

Carbon utilization efficiency can be measured by continuous monitoring of CO_2 in the stack. However, if a metal carbonate (limestone or dolomite) is used for sulfur sorption, the results can be distorted, because CO_2 released during calcination disturbs the mass balance calculations. For example, Lowellville limestone is 90.4 percent $CaCO_3$; in a molar balance during combustion and sorption in an FBC unit, carbon from the limestone accounts for 4.45 percent of the total combustible carbon input to the bed (Babcock and Wilcox Company, 1979).

Nitrogen Oxide Reduction--

Figure 10 shows that most NO_x production from operating experimental FBC units is below the current EPA New Source Performance Standards. Data from PFBC units suggest that they will produce even less NO_x than AFBC units, but neither should have trouble meeting EPA's proposed reductions in the standards. The high NO_x emissions shown in Figure 11 were apparently generated by a carbon burn-up cell (Henschel, 1977).

The factors affecting nitrogen emissions from FBC processes are many and complex. Simply reducing temperatures in the combustion chamber will minimize the thermal formation of NO_x, although careful analysis has shown that the majority of nitrogen emissions result from bound nitrogen in the coal (Mitchell, 1976; Hozio et al., 1977). Therefore, careful manipulation of various process design parameters will be required to keep NO_x emissions below any required limits.

In addition to combustion temperature, design parameters affecting NO_x production are: pressure, gas residence time, excess air, calcium/sulfur ratio, water vapor, carbon monoxide concentration, and char presence. Figure 12 shows a reduction in NO_x emissions as the calcium/sulfur ratio increases in an AFBC unit (Jarry et al., 1970), but this correlation is not apparent in PFBC units. Figure 13 shows that longer gas residence time lowers NO_x emissions (Jarry et al., 1970). Figure 14 (Keairns et al., 1975) shows that nitrogen oxide emissions increase with increasing excess air, which increases the oxygen concentration.

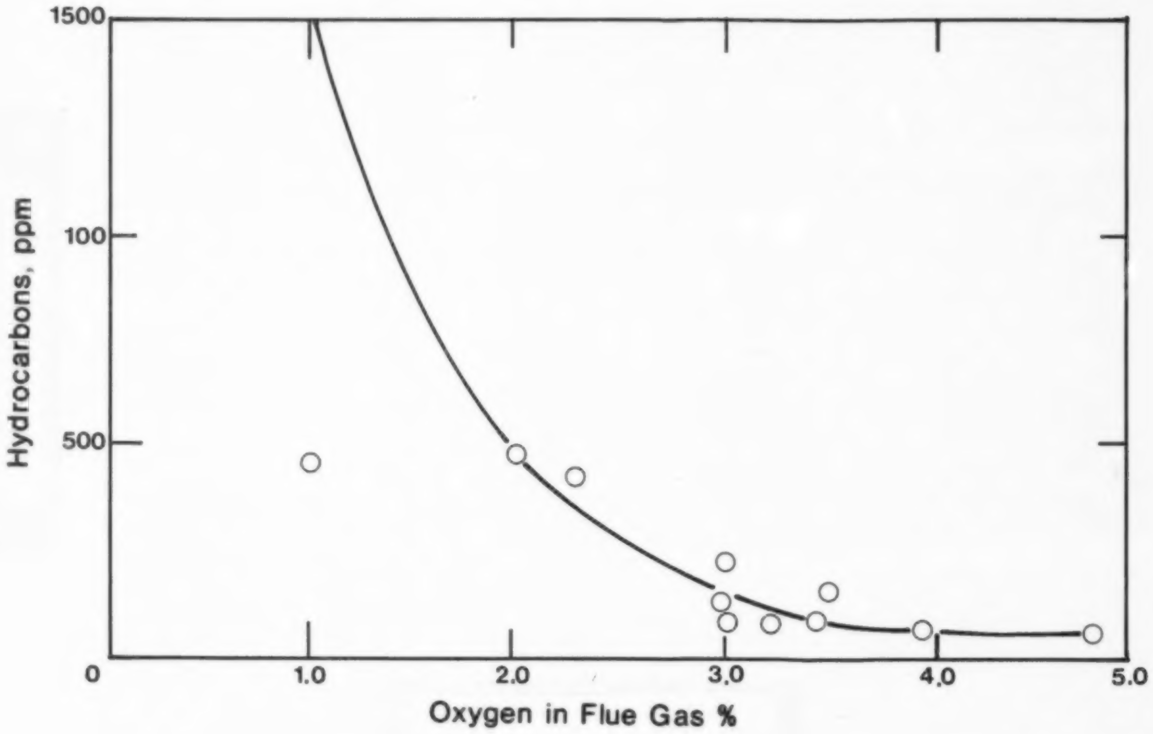


Figure 10. Effect of oxygen concentration on hydrocarbon emission.

(Glenn and Robison, 1970)

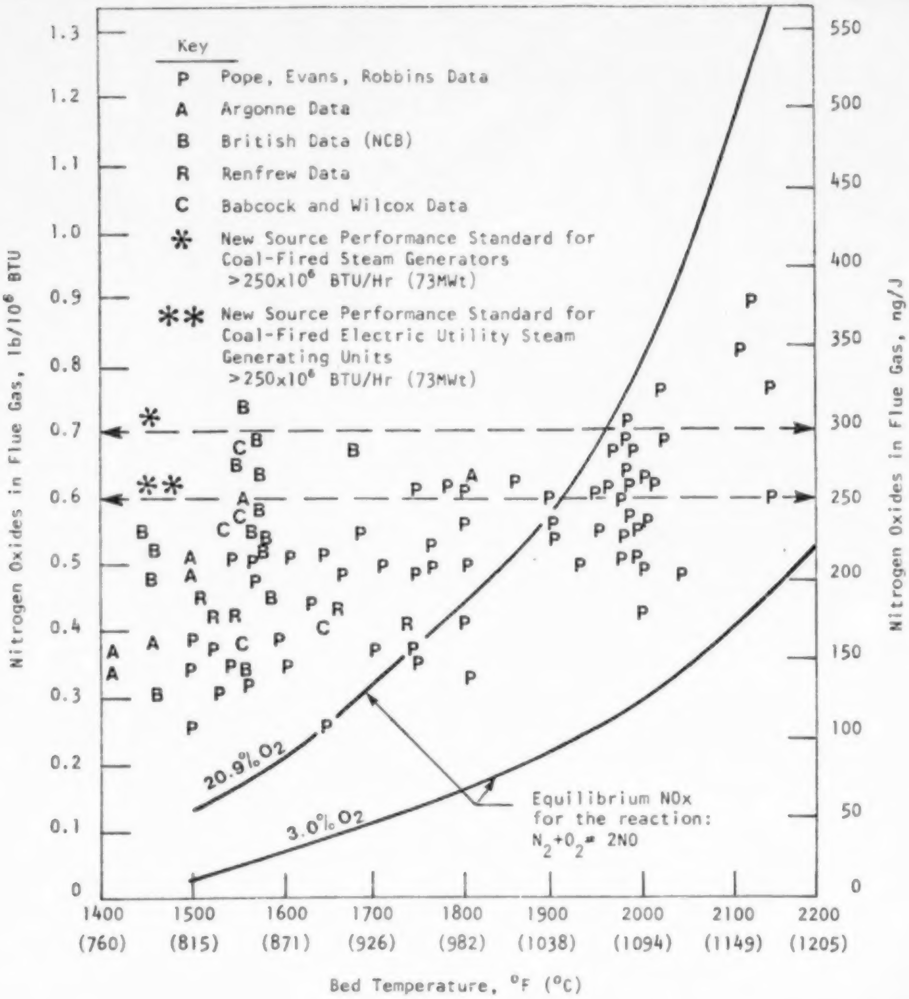


Figure 11. Nitrogen oxides emissions (expressed as NO_2) AFBC units.
(Weber, 1970)

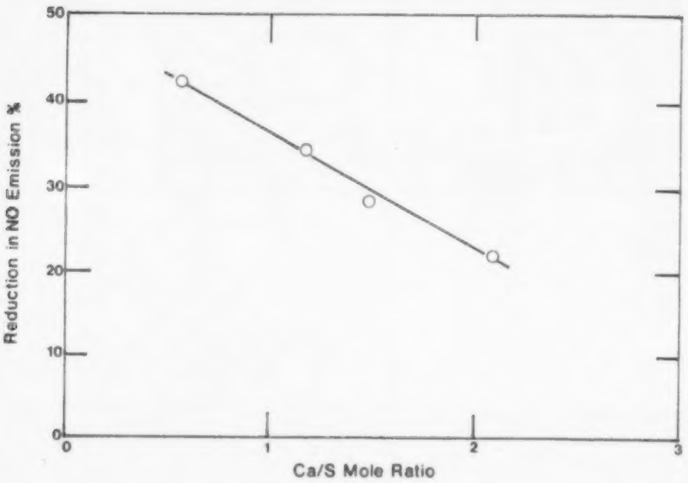
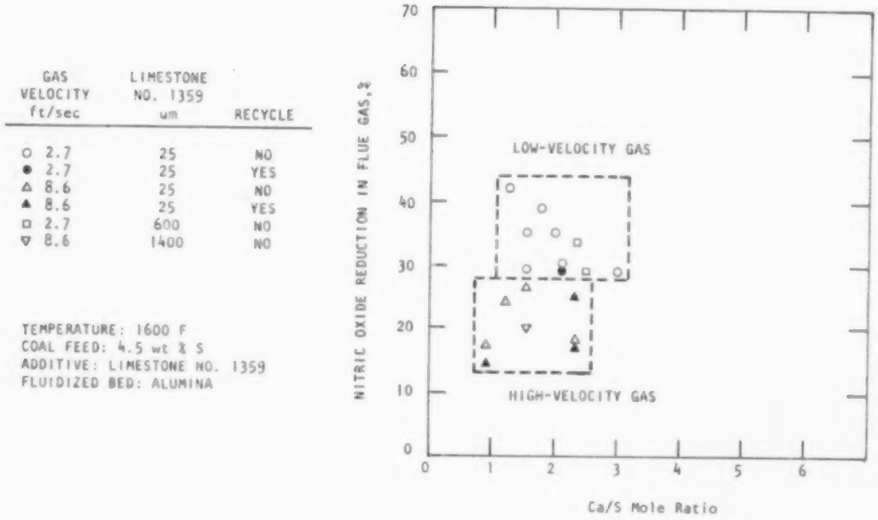


Figure 12. Nitric oxide reduction with -325 mesh (<44um) tymochtee dolomite.

(Jarry et al., 1970)



GAS VELOCITY ft/sec	LIMESTONE NO. 1359 um	RECYCLE
○ 2.7	25	NO
● 2.7	25	YES
△ 8.6	25	NO
▲ 8.6	25	YES
□ 2.7	600	NO
▽ 8.6	1400	NO

TEMPERATURE: 1600 F
COAL FEED: 4.5 wt % S
ADDITIVE: LIMESTONE NO. 1359
FLUIDIZED BED: ALUMINA

Figure 13. Effect of gas velocity on nitric oxide reduction in flue gas .

(Jarry et al., 1970)

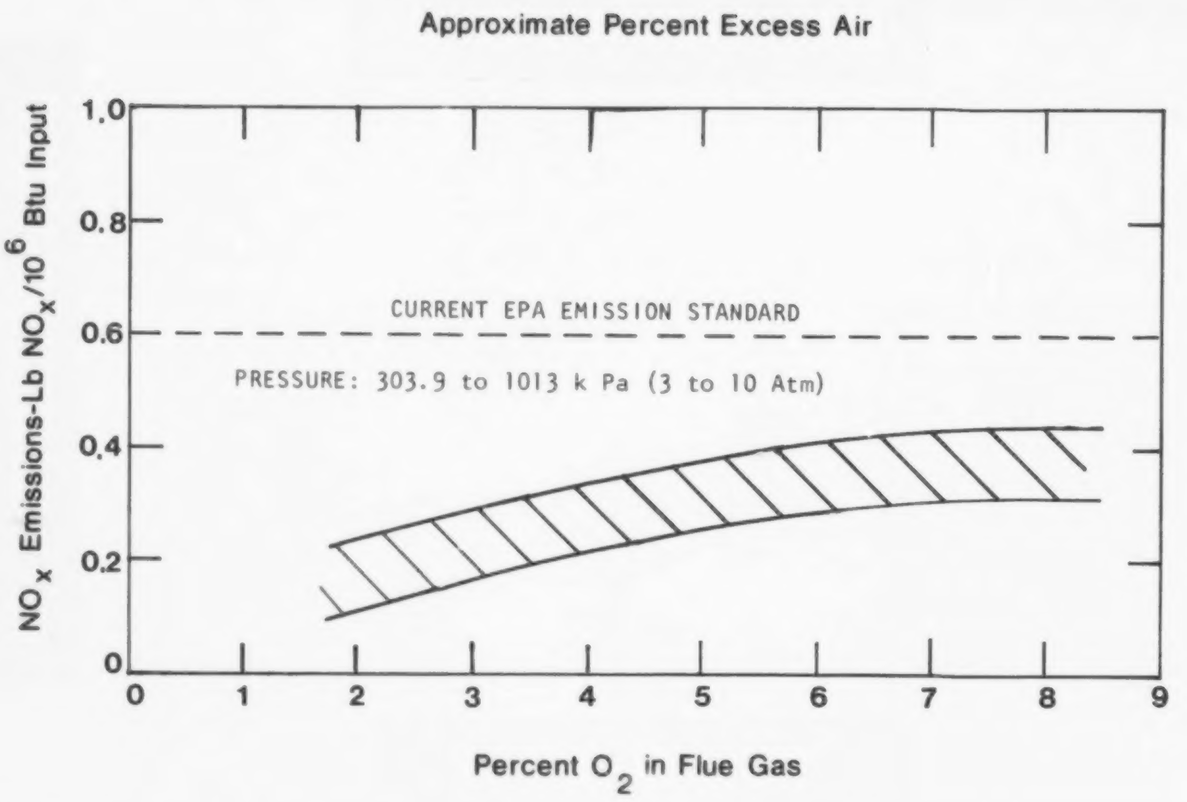


Figure 14. Composite plot of data for NOx emissions from FBC of coal.

(Keairns et al., 1975)

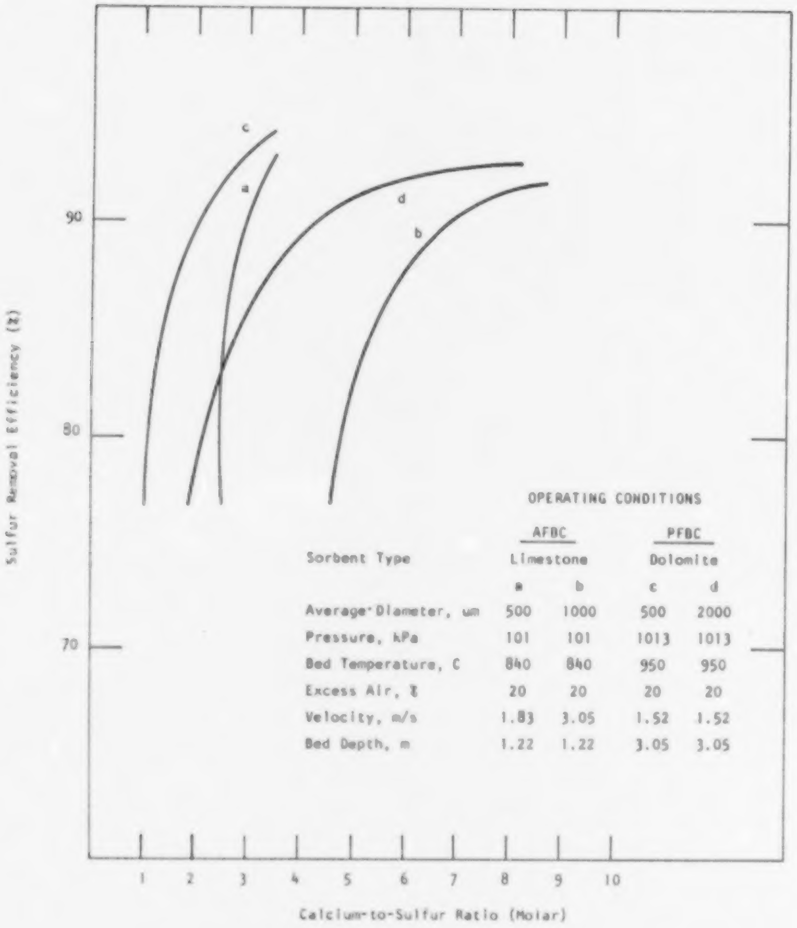
In one experiment attempting to reduce the NO_x output, decomposition catalysts (aluminum and zirconium oxides) were added to the fluidized bed but had no effect. Another catalyst, cobaltous-cobaltic oxide, increased NO_x emissions (Jarry, et al., 1970).

Studies on NO_x formation have shown that the oxides are formed initially in high concentrations near the distributor plate at the bottom of the fluidized bed and decrease in the freeboard area (Pereira et al., 1976). This lower concentration is probably a result of char NH_3 catalyzation of NO to N_2. Utilization of this finding requires some design changes in FBC units to introduce the first cyclone catch onto the top of the fluidized bed. Alternatively, a second shallow uncooled bed could be established where some coal and the recycled char is introduced. The design also requires the introduction of some secondary air into the freeboard (Beer et al., 1977).

Sulfur Dioxide Reduction--

Desulfurization and other sulfur reduction methods can significantly lower sulfur dioxide (SO_2) formation and emission. Desulfurization involves a competition between trapping SO_2 in the bed via chemical reaction and removal from the bed by the fluidizing air following sulfur oxidation. The balance between these two processes is dependent on a multitude of design and operating conditions, such as temperature, bed depth, and gas velocity. When limestone ($CaCO_3$) is used as the sorbent material, other variables must be considered. Different limestones exhibit different absorption rates and capacities, and all require calcination either in the fluid bed or prior to feeding into the combustor. Figure 15 shows several projected sulfur removal curves based on thermogravimetric analyses (Newby et al., 1978), and a kinetic model developed by Westinghouse. To meet the projected EPA standard of sulfur removal, operating conditions must be optimized to maintain low calcium/ sulfur ratios using limestone as a sorbent. High calcium/sulfur ratios require larger quantities of limestone, thereby increasing expenditures for raw materials, for solids disposal, and for capital costs, and also reducing thermal efficiencies. Figure 16 shows several calculated thermal efficiency curves for various calcium/sulfur ratios in a fluidized bed fired with coals containing different sulfur content. These thermal efficiencies can be compared to a thermal efficiency of about 35 percent attained by a conventional pulverized coal combustion plant with flue gas scrubbing.

Calcination conditions have varying effects on sulfur sorption. Pore size appears to be a critical, if not the limiting, factor when using limestone or dolomite as



OPERATING CONDITIONS

	AFBC		PFBC	
Sorbent Type	Limestone		Dolomite	
	a	b	c	d
Average Diameter, um	500	1000	500	2000
Pressure, kPa	101	101	1013	1013
Bed Temperature, C	840	840	950	950
Excess Air, %	20	20	20	20
Velocity, m/s	1.83	3.05	1.52	1.52
Bed Depth, m	1.22	1.22	3.05	3.05

Figure 15. Sulfur removal performance for typical sorbents (projected using Westinghouse kinetic model).

(Newby et al., 1978)

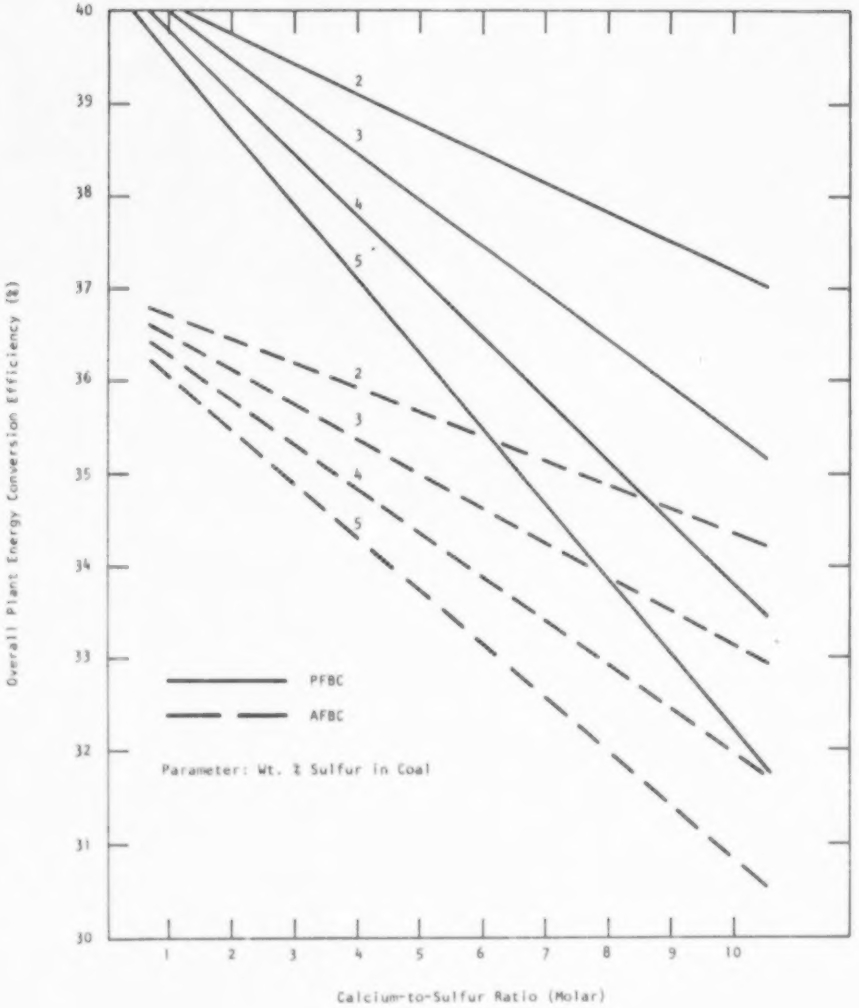


Figure 16. FBC power plant energy conversion efficiency.
(Newby et al., 1978)

sorbents. Salt added to the bed mixture reduces the calcium/sulfur ratio needed to meet standards. Salt appears to cause an increase in the amount of $CaCO_3$ converted to CaO through changes in the pore structure (Gasner et al., 1977). Salt, however, creates other problems, such as corrosion, and is not recommended for addition. Precalcination in a controlled atmosphere changes the limestone sufficiently such that thermogravimetric analysis predicts decreases in the amount of limestone needed for sorption as shown in Table 24. This may not have influence in the design of a small FBC combustor, but in a large plant precalcination may be important and add another step in the process design (Babcock and Wilcox Company, 1979) (Figure 17).

TABLE 24. PREDICTED Ca/S REQUIREMENTS FOR THE ATMOSPHERIC FLUIDIZED BED COMBUSTOR
(Newby et al., 1979)

	Coals	
Sorbents	Eastern coal at 85% S retention	Western coal[a] at 83.3% S retention, corresponding to 0.2 lb SO_2/M.Btu
Raw Greer Limestone	2.5	0.83
Precalcined Greer	1.7	0.57
Raw Grove Limestone	5.7	2.0
Precalcined Grove	2.0	0.58

[a] The ash CaO utilization is assumed to be 30%.

The chemical reaction rate limiting step in sulfur sorption appears to be the oxidation of SO_2 to SO_3 prior to calcium sulfate formation. This step may be catalytically enhanced by compounds found in coal, by limestone, or by added catalysts. Analysis of spent bed material showed large amounts of iron in the sulfated layer indicating that iron may be a catalyst for sulfur uptake (Yang et al., 1978).

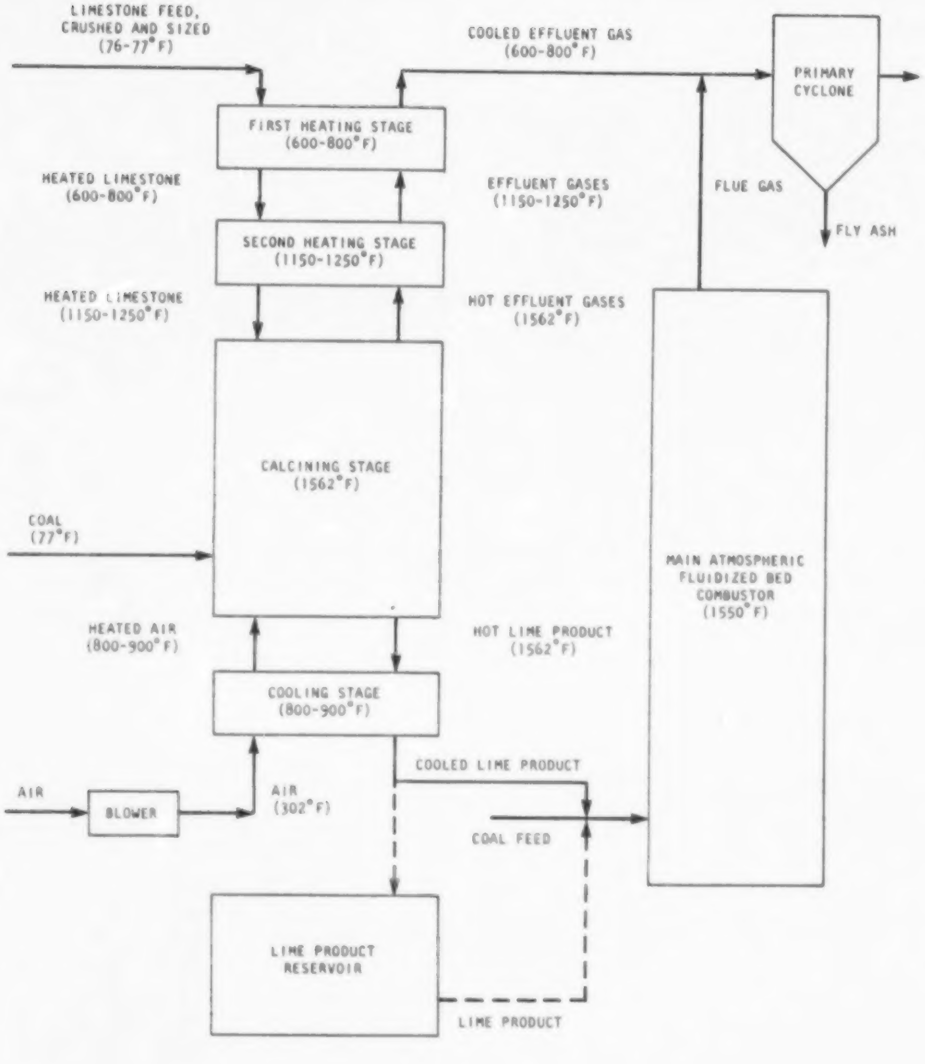

LIMESTONE FEED, CRUSHED AND SIZED (76-77°F)
COOLED EFFLUENT GAS (600-800°F)
PRIMARY CYCLONE
FIRST HEATING STAGE (600-800°F)
HEATED LIMESTONE (600-800°F)
EFFLUENT GASES (1150-1250°F)
FLUE GAS
FLY ASH
SECOND HEATING STAGE (1150-1250°F)
HEATED LIMESTONE (1150-1250°F)
HOT EFFLUENT GASES (1562°F)
CALCINING STAGE (1562°F)
COAL (77°F)
MAIN ATMOSPHERIC FLUIDIZED BED COMBUSTOR (1550°F)
HEATED AIR (800-900°F)
HOT LIME PRODUCT (1562°F)
COOLING STAGE (800-900°F)
COOLED LIME PRODUCT
AIR
BLOWER
AIR (302°F)
COAL FEED
LIME PRODUCT RESERVOIR
LIME PRODUCT

Figure 17. Schematic flow diagram of the precalcination process.

Particulate Matter--

In 1977, fly ash produced by coal-fired power plants was considered to be the sixth most abundant mineral in the United States (Chemical and Engineering News, 1978). FBC processes will produce even more non-sintered solid material than the conventional coal-fired power plants. Particulate matter is derived from char, ash, and from sulfur sorbent material in the fluidized bed, and each group has different physical and chemical characteristics. The mechanisms controlling the formation of the particulate matter during process are related to a number of variables. The major variables are fluidizing velocity, feed material particle size, feed material distribution and feed rates, degradation rates of the bed material, interparticle attrition rates and buoyancy, and bed geometry and height, including the height of the freeboard. The majority of particulates in FBC processes are derived from the sorbent material, with the total quantity being dependent on the calcium/sulfur ratios required to meet sulfur removal performance standards (Newby et al., 1979). Figure 18 shows calculated particle loadings for a calcium/sulfur ratio of 2, compared to actual values obtained in a combustor: a total loading of 0.535 gm solids produced per gram of coal. Table 25 shows some of the physical parameters of flue gas particulates from a PFBC unit.

The release of particulates through the stack to the atmosphere is a function of the final particulate removal system performance as shown in Figure 19. The very small particulates (less than 3 microns) are significant because they easily adsorb toxic elements and are respirable into the human lungs.

OUTLOOK

It is relatively certain that FBC will be commercialized; the timetables for market entry, however, will depend on various technical, economic, environmental and political factors. Technical factors weigh heavily in making a choice and commitment to either AFBC or PFBC or both. Technically, they are both good choices. Each offers certain advantages, over its range of applicability.

Some companies such as Pope, Evans & Robbins, Inc., Combustion Engineering, and Babcock and Wilcox, Alliance, Ohio, are concentrating entirely on atmospheric systems; others such as Curtiss-Wright Corp. and Exxon are concentrating on pressurized systems. Still others, such as Babcock & Wilcox Ltd., London, are actively involved in both lines of development (McKenzie, 1978). Companies pursuing both lines feel that AFBC will be preferred for industrial-sized boilers, and that utilities will prefer pressurized systems, which can

TABLE 25. PROPERTIES OF THE PARTICLES SUSPENDED IN THE FLUE GAS (Murthy et al., 1977)

<1 micron	7% wt.
1 to 3 microns	39% wt.
3 to 10 microns	21% wt.
>10 microns	33% wt.
Predominant shape:	Irregular
Evident cleavage:	None
Structure:	3 phase
Color:	White, black, red

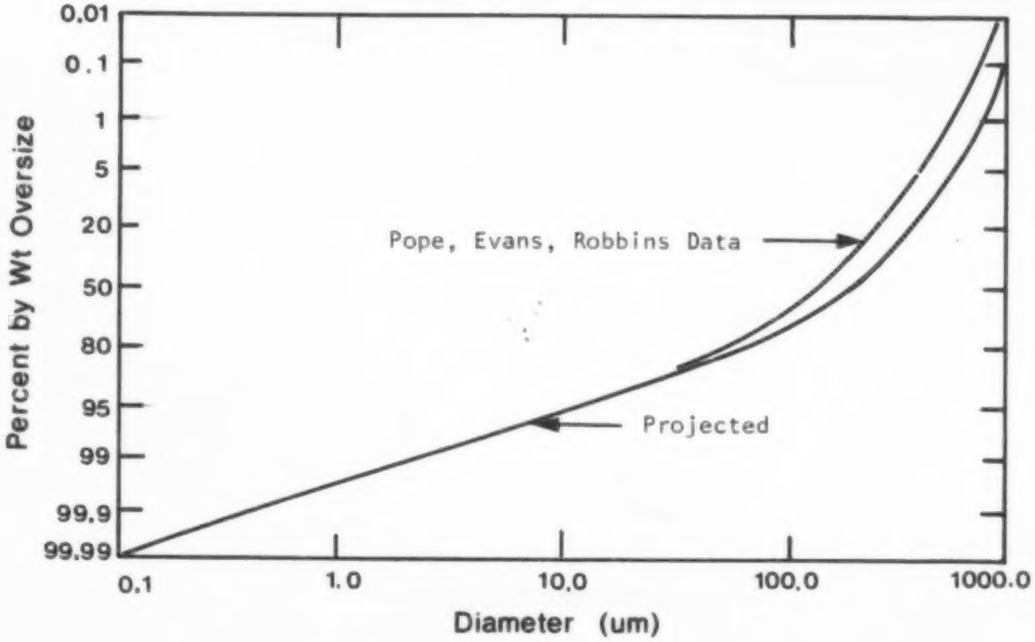


Figure 18. Total solids from combustor (AFBC).

(Newby et al., 1978)

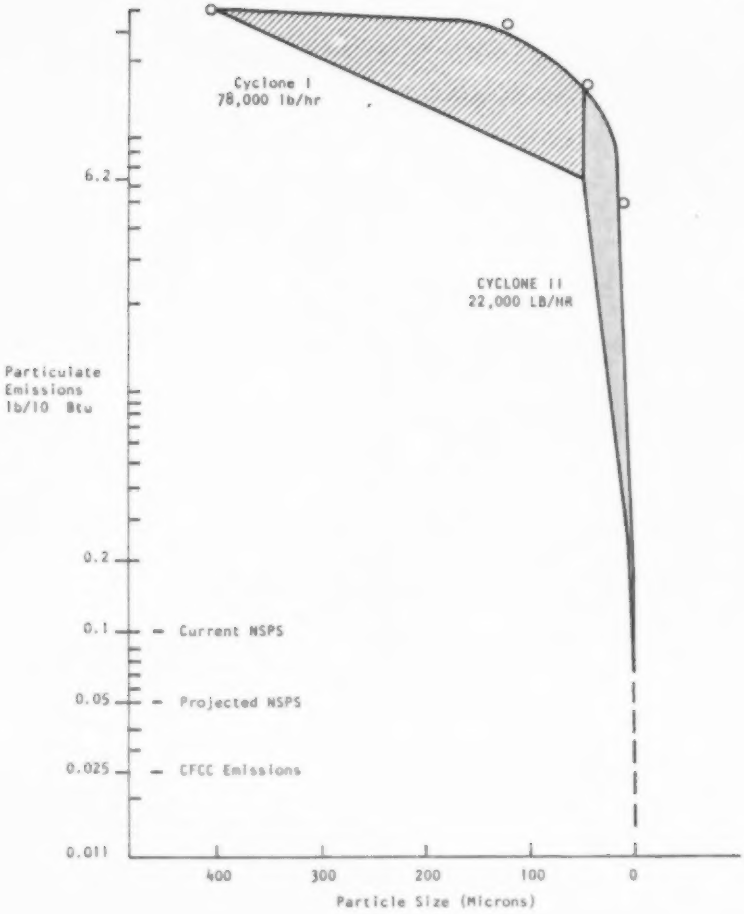


Figure 19. CFCC particulate emissions.
(Lucke and Murphy, 1977)

be adapted to combined-cycle use. For a large utility plant generating about 200 megawatts, important capital-cost savings will be realized by the PFBC's smaller size and improved efficiency is achieved through combined cycles.

The controversy on timing stems from uncertainty as to scale-up and the usefulness of pilot-plant data. Some United States research laboratories conduct exhaustive small-scale investigations on emissions and their control, sorbent behavior, and other fluidized-bed phenomena. Others, especially European firms, insist that small-scale results will not apply to scaledup units. Researchers from such companies, including Stal-Laval Turbin (Finspong, Sweden) and Babcock & Wilcox Ltd. (London), feel that enough data already exist to permit construction of major prototype facilities.

A different opinion is held by those involved in a Pressurized FBC demonstration plant to be built at Grimethorpe, England, by the British Government's National Coal Board. The 80 megawatt (thermal) unit will be of prototype size but will be used purely for research. It is expected to be more flexible than a commercial unit and should better lend itself to full-scale experimentation.

Researchers at Grimethorpe doubt there are enough relevant data available to successfully design and operate full-scale, pressurized fluidized bed combustor/gas-turbine systems. However, Stal-Laval Turbin and Babcock & Wilcox researchers, among others, disagree. The Grimethorpe team consider it premature to tackle both the problem of a pressurized fluidized bed combustor and that of coupling such a combustor to a gas turbine. Some US experts feel that the Stal-Laval/Babcock & Wilcox team is overlooking the problems of gas-turbine-blade erosion/corrosion due to sodium, potassium and vanadium in the coal.

One project, already considered obsolete by some, is the 30 megawatt (electrical) prototype atmospheric unit, built in Rivesville, West Virginia, by Pope, Evans & Robbins for the former U.S. Office of Coal Research, now part of U.S. Department of Energy (DOE). The project was an attempt to develop a relatively inexpensive coal-fired boiler for power generation. Contracted for in 1972, before the coal price-rise, the system was designed to compete with oil-fired boilers. The plant is a multi-cell FBC unit, consisting of four separate beds. The first bed boils the water, the second heats the resulting steam, the third superheats the steam, and the fourth burns up unburned carbon. Problems have been encountered, particularly with coal-handling and coal-feed systems. One persistent problem is clogging of coal in feed lines, blocking the fuel supply.

Fluidized bed combustors must compete economically, not with oil-fired boilers, but with conventional coal-fired boilers using scrubbers. Pope, Evans & Robbins researchers concede that times and priorities have changed. However, the company questions a wholesale switch to PFBC, believing that money saved by smaller size units for the same output (pressurized unit) will be offset by the additional cost of coping with higher pressures, especially for feeding coal and removing solid waste. Pope, Evans & Robbins researchers feel that atmospheric systems are preferable for all size ranges.

Stal-Laval researchers believe that pressurized systems may be preferable to medium or large-scale FBC applications. The firm cites the advantage of being able to double a pressurized system's useful energy output by using combined cycles or cogeneration. Its researchers believe this will be the most effective lever in persuading industries to convert their boilers to ones that use pressurized fluidized bed coal firing.

Dr. Steve Freedman, Director of the U.S. DOE's fluidized bed program, feels that industrial-sized AFBC units are closest to becoming commercial. Their greatest advantage, he believes, is their fuel-use flexibility. Freedman sees utility systems as a longer term proposition. DOE hopes to have both large AFBC and large PFBC plants on-line by 1984, so utilities can choose between the two systems. There are advantages in both approaches: atmospheric is simpler and more reliable, while pressurized has a slightly higher efficiency and produces slightly fewer sulfur-dioxide emissions.

Other differences of opinion exist. Columbus Battelle and various U. S. researchers are concerned about possible corrosion of boiler tubes. Others, especially those in Europe, see nothing at all to suggest that such problems will arise (McKenzie, 1978).

A number of factors inhibit the introduction of FBC technology. Initially, the air pollution rules favor the use of clean fuels such as natural gas and low sulfur fuel oil. As the price of these fuels rise, there will be a shift to coal where fluidized bed combustors must compete with established technology and add-on flue gas desulfurization.

Another problem arises from the fact that FBC is an untried technology. While it is agreed that FBC solves the SO_x and NO_x problems, it is unknown whether new pollutants in low concentration will be generated. Coal contains many impurities, and these compounds may be released into the environment. The little available evidence from research units does not suggest any hazard, but these units have not been adequately tested and the problems of scale-up to commercial units remain to be examined. Additionally, governmental regulations are constantly changing with unknown consequences for FBC technology. As one person at Babcock & Wilcox said, "There are hundreds of orders for the second commercial combustor built."

The remainder of the problems are economic. There is little governmental economic incentive to develop and commercialize FBC. The federal government has approved the release of low interest bonds to finance pollution control equipment; however, these bonds can be used to finance the installation of scrubbers on existing conventional coal burning facilities, they cannot be used to finance new FBC installations which are not designed as a basic principle to emit no pollution. Also, these bonds cannot be used to convert existing coal-burning facilities with pollution problems to FBC processes. These negative governmental measures could substantially retard FBC development.

From a large utility standpoint, there appears to be little incentive for FBC technology. While it appears that fluidized bed combustors are more energy-efficient than conventional combustion with add-ons, there is little incentive to switch as many state utility regulators permit fuel cost pass on or recovery. Also, allowance is made for capital recovery for equipment, and thus, there is little incentive to build cheaper plants. Where utilities cannot recover their costs (e.g., employee salaries), they are already pared to the bone. Table 26 shows the wide variety of factors influencing the commercialization of any new or emerging technology, such as FBC.

Despite these problems, it seems fairly certain that FBC of coal will be commercialized. It is probable that the first units installed will be small industrial boilers. The timetables are uncertain since they depend on technical, economic, environmental and political factors. Because of their technological complexity, pressurized systems will undoubtedly be commercialized after atmospheric units.

TABLE 26. FACTORS INFLUENCING THE COMMERCIALIZATION OF FLUIDIZED BED COMBUSTION OF COAL

Influence factor	Degree of current quantification	Degree of influence on commercialization
A. ECONOMIC FACTORS		
1. Benefit/costs	++	+++
2. Availability of Commercial Scale Components	+++	+++
3. Number of Existing Units	+++	++
4. Existing Unit Size vs Commercial Unit Size	+++	++
5. Commercialization Schedule (DOE Industrial Foreign)	+++	++
6. Potential Market Size	+++	+++
7. US Government R&D Support	+++	+++
B. ENVIRONMENTAL FACTORS		
1. Relative Known Hazard	++	++
2. Number of Waste Streams	+++	?
3. Pollutant Mass Flow Rate	+++	?
4. Extent and Types of Fugitives	++	++
5. Relative Effectiveness of Existing Controls	++	++
6. Variability of Emissions with Site	+0	+++?
7. Availability of Environmental Baseline Information	+0	?
8. Availability of Commercial Monitoring Equipment	++	?
C. POLITICAL/INSTITUTIONAL FACTORS		
1. Perceived Relationships to National Energy Needs	+0	+++
2. Current and Anticipated Tax Advantages	++	++
3. Regional Differences in Advocacy and Commitment	+++	++
4. Historical Industrial Preference	+++0	++
5. Perceived Short Term and Long Term Advantages	++	++
6. Regulatory Constraints	+++	+++
7. Regulatory Incentives	+++	++
D. TECHNICAL FACTORS		
1. Magnitude of Unresolved Technical Problems (i.e., coal feed)	++	+++
2. Process Differences	+	+
3. Raw Material Acquisition	++	+++
4. Simplicity vs Complexity of Process/Technology	+0	?
5. Professional Opinion and Preference	+0	+++?

High Degree	+++
Moderate Degree	++
Slight Degree	+
Unknown	?
Extremely Difficult to Estimate	0

SECTION 3

SELECTION OF POLLUTANTS FOR MONITORING

INTRODUCTION

The EPA is interested in monitoring pollutants from coal facilities utilizing FBC primarily to support pollution control and abatement efforts, promote compliance with standards, and protect public health and welfare. The advances made in the understanding of the complex manner in which pollutants may impact human and environmental receptors have led the EPA to develop holistic approaches to assessment and monitoring (Cleland and Kingsbury, 1977; Schalit and Wolfe, 1978; Behar et al., 1979).

Since it is reasonable to assume that a commercial-scale fluidized bed combustor may emit some unregulated pollutants, selecting pollutants for monitoring is difficult. However, monitoring both regulated and unregulated substances may support research designed to link a source to known impacts or health and ecological effects. A serious deficiency in current approaches to monitoring is the absence of an organized procedure for selecting pollutants to be included in a monitoring program. In this section, a conceptual framework is developed for such a procedure, as part of an approach to the design of a source-oriented ambient monitoring program.

Objectives of a source-oriented ambient monitoring program may include monitoring to:

- Assure compliance with existing standards, criteria and regulations addressing source emissions, receptor media, and potential environmental effects
- Support effects monitoring and research
- Accumulate baseline data in anticipation of proposed standards, criteria and regulations
- Verify dispersion/transport models
- Add to existing data banks holding environmental data

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Monitoring objectives provide the rationale for identifying:

- Which type of pollutants need to be monitored
- Where monitoring should be done in relation to the source
- Where sampling sites should be located in the environment
- How frequently samples should be collected
- How monitoring data should be analyzed
- The format in which results of analysis and raw data are reported
- The quality assurance requirements
- Analytic methods selected for ambient measurements

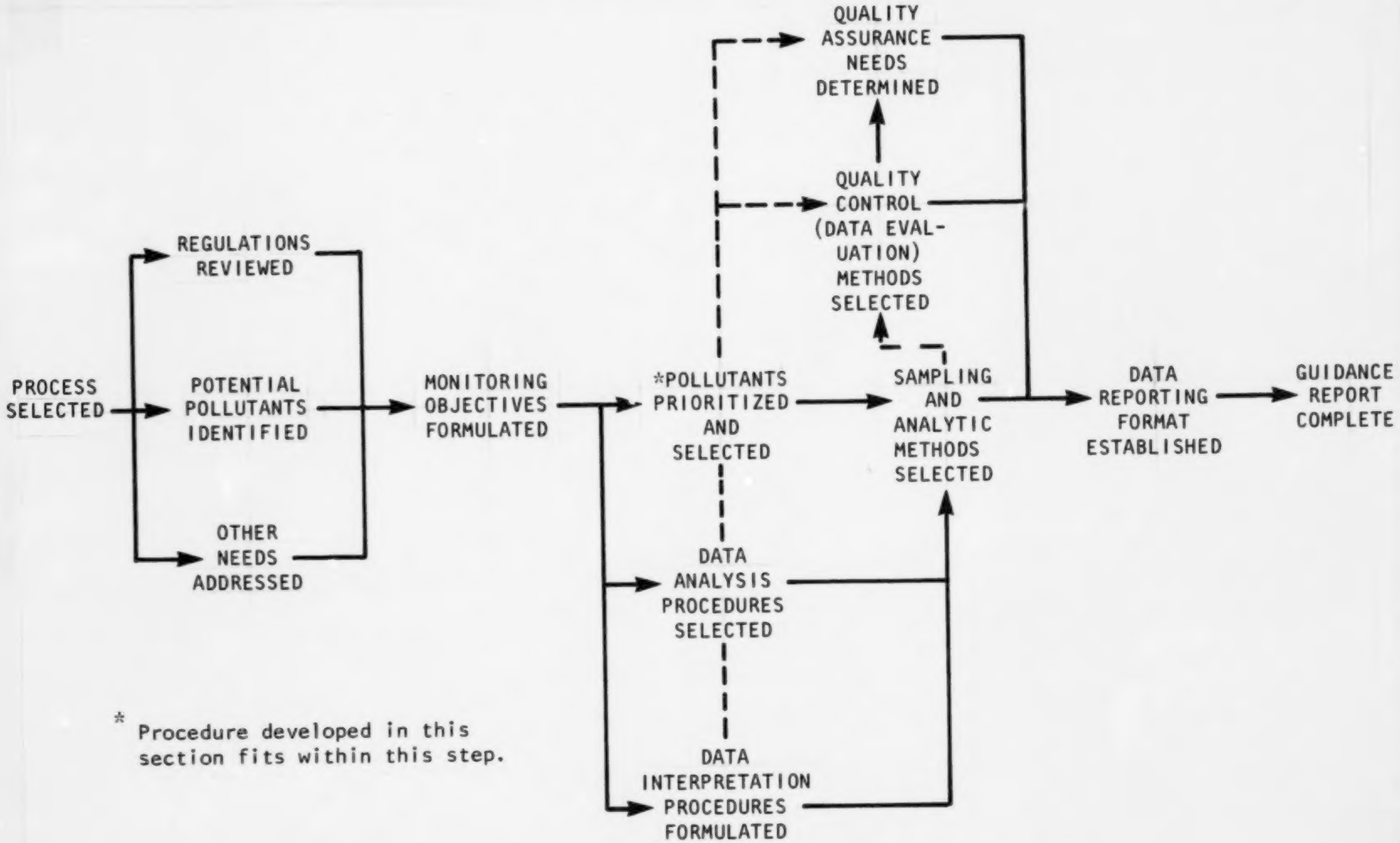
The objectives determine the overall perspective and details of every element of the monitoring program. Therefore, they must be made explicit at the beginning of the design process to assure that the objectives will be met after the effort is completed.

As Figure 20 illustrates, before the prioritization procedure can be used, candidate pollutants and monitoring objectives are identified. Data analysis and quality control needs to meet program objectives are formulated concurrently with the selection of pollutants that are to be monitored. Once the pollutants have been selected for the program, sampling and analytic methods can be considered. Ideally, the entire monitoring program should be designed before any actual sampling begins.

The specific monitoring objectives used to illustrate how the proposed pollutant selection scheme works include monitoring to:

- Assure compliance with existing federal standards, criteria, and regulations exclusive of Occupational Safety and Health Act (OSHA)
- Accumulate baseline data in anticipation of proposed standards criteria and source regulations
- Support effects monitoring and research

Monitoring program objectives influence the pollutant selection process by providing the basis for identifying the



PROCESS SELECTED
REGULATIONS REVIEWED
POTENTIAL POLLUTANTS IDENTIFIED
OTHER NEEDS ADDRESSED
MONITORING OBJECTIVES FORMULATED
*POLLUTANTS PRIORITIZED AND SELECTED
DATA ANALYSIS PROCEDURES SELECTED
DATA INTERPRETATION PROCEDURES FORMULATED
QUALITY ASSURANCE NEEDS DETERMINED
QUALITY CONTROL (DATA EVALUATION) METHODS SELECTED
SAMPLING AND ANALYTIC METHODS SELECTED
DATA REPORTING FORMAT ESTABLISHED
GUIDANCE REPORT COMPLETE

* Procedure developed in this section fits within this step.

Figure 20. Design of an ambient monitoring program.

series of questions that must be asked during the selection process. Once these questions are identified, they are organized so an efficient and systematic selection procedure results. This approach also lends itself to careful documentation of the entire program design.

Initially, the questions used to determine whether a substance required monitoring were identified. Relationships among the questions were reviewed and dependencies established. The dependencies were utilized to organize the questions into a hierarchy that represents a logical flow from identification of the chemical nature of a substance to a determination that its concentration should be monitored in the ambient environment. The procedure attempts to achieve objectives:

- Categorization of all potential pollutants
- Priority ranking of FBC pollutants
- Selection of regulated and problem pollutants for monitoring in the ambient environment

The first objective of the procedure is to categorize the candidate pollutants into three types based on the monitoring objectives of the program:

- Those that must be monitored in the ambient environment or facility effluent according to existing legal requirements (Category I pollutants)
- Those that could be monitored based on proposed regulations or criteria (Category II pollutants)
- Those for which there are no existing or proposed regulations or criteria (Category III)

Unregulated pollutants that are likely to present a serious hazard to human health and welfare are included in Category I during implementation of the procedure. Category I pollutants are the minimum set of pollutants to be included in the monitoring program, unless cost or other considerations make this unreasonable. This approach assures that legal requirements for monitoring are met and potentially significant health and ecological problems are considered. Monitoring of Category II pollutants is desirable but not required. Design of a monitoring program should include monitoring for these substances in anticipation of future needs to meet standards currently proposed or pending.

The second objective is to priority rank the Category III pollutants to decide which unregulated substances need monitoring. Some existing threshold criteria for Category III pollutants are identified in available literature; new criteria may be derived from a review of known health and ecological effects. Ideally, the threshold criteria represent a tentative level of concentration in the environment below which significant adverse effects are unlikely. This concentration is used as a basis for ranking the hazard potential of the pollutants prior to selecting those designated for monitoring.

The third objective is to select the pollutants to be monitored. This set of substances will include, minimally, Category I pollutants and their support parameters. Support parameters are the environmental characteristics which are not associated with selecting sampling sites and frequency, but are needed in order to interpret whether a standard or criterion is met or exceeded. Typical support parameters are temperature, wind velocity and direction, and stream or aquifer flow rate. In addition, Category II substances and the most hazardous substances in Category III should be included in the program. The outcome is a list of pollutants that will not be monitored and a list of those that will be monitored to meet specific monitoring program needs. A summary list of the pollutants in the former group is retained to document the decision process used in selecting the pollutants for monitoring.

The hierarchical organization of the procedure is illustrated in Figure 21. The discussion in this section presents this systematic approach to the selection of the pollutants for monitoring in the ambient environment.

ASSUMPTIONS

The procedure is designed for application to a specific FBC process selected as the focal point of a source-oriented ambient monitoring program. The FBC process is assumed to include all activities associated with combustion of coal at a particular facility, from moving coal and sorbent from a storage pile on-site, to disposal of all wastes at an approved landfill. Basic assumptions are:

- A review of the literature on the FBC technology has been completed.
- Sufficient information on starting materials and effluents from pilot demonstration, and all commercial plants is available.
- A specific set of monitoring objectives guide development of the monitoring program.

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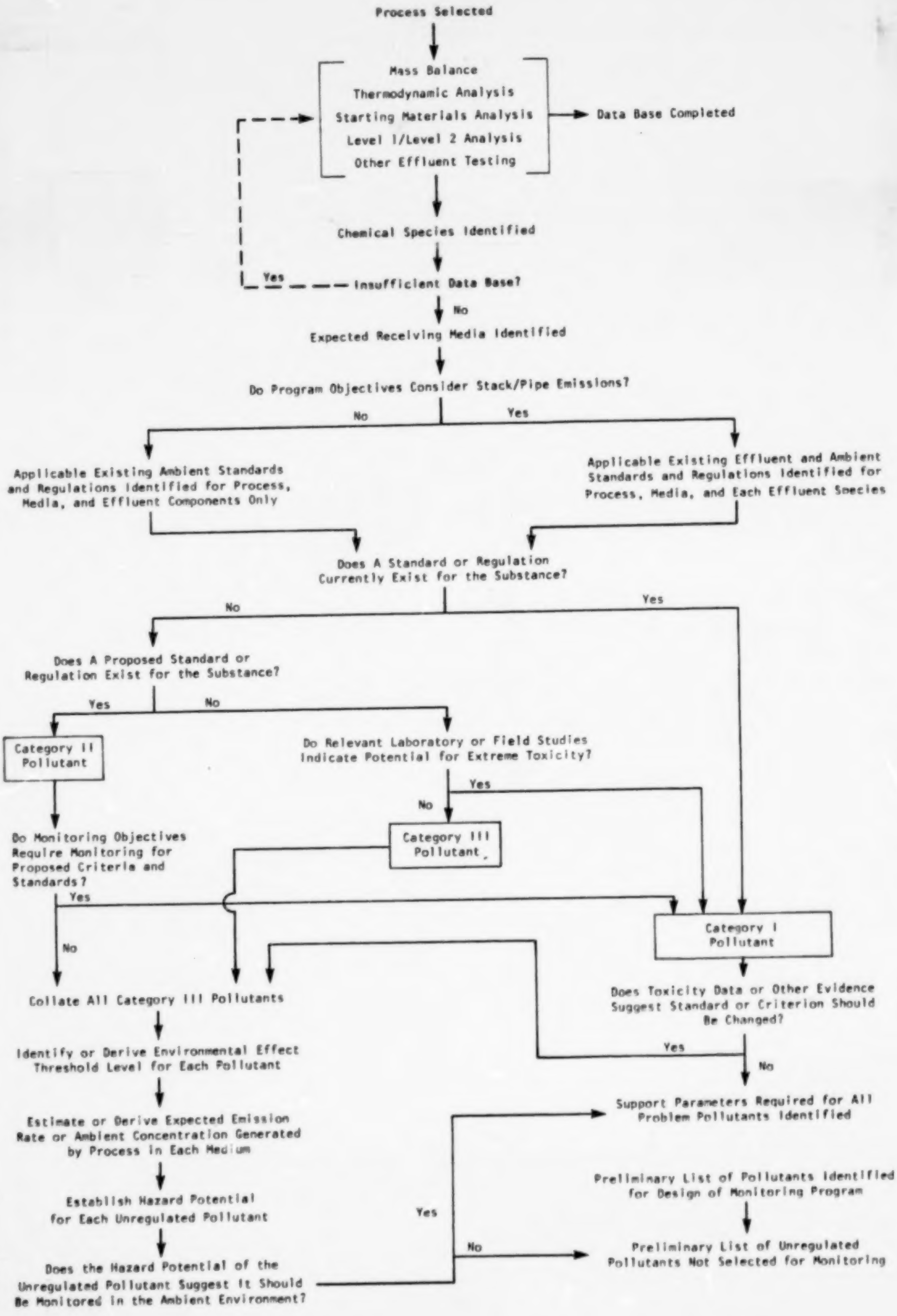
Process Selected
Mass Balance
Thermodynamic Analysis
Starting Materials Analysis
Level 1/Level 2 Analysis
Other Effluent Testing
Data Base Completed
Chemical Species Identified
Yes
Insufficient Data Base?
No
Expected Receiving Media Identified
Do Program Objectives Consider Stack/Pipe Emissions?
No
Yes
Applicable Existing Ambient Standards and Regulations Identified for Process, Media, and Effluent Components Only
Applicable Existing Effluent and Ambient Standards and Regulations Identified for Process, Media, and Each Effluent Species
Does A Standard or Regulation Currently Exist for the Substance?
No
Yes
Does A Proposed Standard or Regulation Exist for the Substance?
Yes
No
Category II Pollutant
Do Relevant Laboratory or Field Studies Indicate Potential for Extreme Toxicity?
Yes
No
Category III Pollutant
Do Monitoring Objectives Require Monitoring for Proposed Criteria and Standards?
Yes
No
Category I Pollutant
Collate All Category III Pollutants
Does Toxicity Data or Other Evidence Suggest Standard or Criterion Should Be Changed?
Yes
No
Identify or Derive Environmental Effect Threshold Level for Each Pollutant
Support Parameters Required for All Problem Pollutants Identified
Estimate or Derive Expected Emission Rate or Ambient Concentration Generated by Process in Each Medium
Preliminary List of Pollutants Identified for Design of Monitoring Program
Establish Hazard Potential for Each Unregulated Pollutant
Yes
No
Preliminary List of Unregulated Pollutants Not Selected for Monitoring
Does the Hazard Potential of the Unregulated Pollutant Suggest It Should Be Monitored in the Ambient Environment?

Figure 21. Procedure for selecting pollutants for a source-oriented ambient monitoring plan.

It is further assumed that:

- Monitoring networks are designed to detect specific substances in the ambient environment around a facility utilizing the FBC process and potential waste disposal sites. Therefore, pollutants generated by a source are priority ranked, in contrast to the priority ranking of sources or facilities (Eimutis, 1976; Reznik et al., 1978; Slawson, 1979; Everett, 1979).
- Adequate information is not available in most cases to establish error associated with estimates of effects and production rate factors of pollutants from the processes considered. Therefore, the approach presented here for identifying the pollutants that should be monitored in the ambient environment cannot produce probability statements indicating the level of confidence associated with the decision that monitoring is required.

CATEGORIZATION

Overview

Categorization of effluent components involves four processes:

1) Identify chemical species in each effluent stream
2) Determine receptor media for each chemical species
3) Identify relevant standards, criteria, and regulations for the facility, effluent streams, media, and individual pollutants
4) Identify extremely hazardous or toxic substances

These four steps divide the initial list of effluent components into three groups, each with different monitoring requirements. It is possible for design of a monitoring program to focus on only one or all of these groups of pollutants.

Species Identification

If there has been extensive analysis of effluents and emissions from pilot and demonstration plants, the list of conceivable pollutants may include single chemical species and families of substances with closely related chemical structures. When a group of closely related chemical species is identified in process effluents, refinement of information on chemical structure and properties of the component is needed so appropriate regulations and health and ecological effects can be utilized in evaluating whether or not monitoring the group's ambient concentration is necessary.

An effluent component which includes a group of closely related chemical substances may be identified, but the information necessary to determine exactly which species is in the effluents can be unavailable. The monitoring requirements with respect to this component would be determined in one of two ways: 1) the component may contain so few species that considering each member of the group for monitoring is warranted; or 2) the component may include a variety of species; however, monitoring the component as a group could be more appropriate. As a third alternative, the group could be broken into subsets, and each subset of the component considered for monitoring. Consideration of available analytical methods is a significant factor in deciding how to proceed.

In the event that the chemical makeup of an effluent component is unknown, completion of a Level 1/Level 2 assessment or other effluent characterization procedures would be recommended before developing a source-oriented ambient monitoring program for the component. Level 1 sampling and analysis is designed to give rough information on the amount of all pollutants for which Multimedia Environmental Goals (MEGs) have been established. Level 2 sampling is a focused, accurate analysis program for a few selected chemical pollutants.

At this point, the best available information on the kinds of pollutants present in process effluents is assembled for further consideration.

Media Determination

Further characterization of an effluent component according to the environmental medium most likely to receive the substance(s) is needed prior to identifying relevant standards and regulations, and potential health and ecological effects. The description of the process selected for monitoring provides the information for determining where the substances are most likely to enter the ambient environment. Otherwise, the receiving media must be assumed, based on whatever information is available on operation of the fluidized bed combustor and disposal methods.

Identification of Standards and Criteria for Specific Chemical Components of the Effluent Streams

Legal requirements for ambient monitoring based on the facility or process type and specific location of the facility are identified first. Next, existing and interim federal environmental laws and regulations relevant to the FBC process are reviewed to determine appropriate standards and criteria for each receptor medium and waste substance. A sample list of these laws, including air, water, and solid waste statutes, regulations, and other environment-related governmental orders, is provided in Appendix B.

Category II pollutants are identified through review of the status of laws which are being translated into regulations. Normally, regulations are proposed, the proposals reviewed by the public, and the proposed rules revised accordingly, before final promulgation. Any applicable proposed regulations are reviewed to identify Category II pollutants. Proposed interim regulations would be considered for identifying Category II pollutants, since they are not currently enforceable (Section 5).

If emission standards are considered in scope, chemical species for which emission rates or discharge are regulated should be placed in Category I even though monitoring in the ambient environment may not be explicitly required. For these substances, monitoring can be used to verify compliance with emission standards in a potentially cost-effective manner.

Any changes, revisions, or amendments to regulations and standards can be identified through review of the Federal Register and secondary sources. In the event that evidence becomes available that a standard or criterion is excessive, deficient, or recently revised, the need to monitor the pollutant can be reconsidered based on the new evidence.

Identification of Extremely Hazardous or Toxic Substances

At this point, both regulated and unregulated pollutants have been identified and characterized according to chemical species and receptor medium. If available evidence indicates that some of the unregulated substances are extremely toxic or hazardous to human or environmental receptors, they can be placed in Category I and automatically considered for monitoring. The implication is, in this case, that discharge of even very small quantities carries some risk to environmental receptors. If data indicate only very small emissions of these substances are expected from the source, the data can be used to support a position that they are unlikely to cause impacts and should not be monitored.

Evidence of extreme hazard can be obtained from two primary sources. Lists can be consulted which reflect attempts by government agencies and other organizations to identify substances posing a threat to health and the environment (International Joint Commission, 1978; Keith and Telliard, 1979). Alternately, the EPA-NIH Chemline can be reviewed to locate toxicological data on substances not on these lists. The open literature can also be used to identify potential hazards of the unregulated pollutants, including acute toxicity, sub-acute or chronic toxicity, persistence, or bioaccumulation.

Using criteria proposed in Table 27, extremely toxic substances in process effluents can be identified.

TABLE 27. CRITERIA USED TO IDENTIFY EXTREMELY TOXIC SUBSTANCES

Type of data available	Threshold level indicating extreme toxicity	Reference
Acute Oral Toxicity, Mammalian LD_{50}	<20 mg/g	Weber, 1977
Acute Ingestion Toxicity, Fish 24, 48 or 96 hr LC_{50}	<0.01 ppm	Weber, 1977
96 hr LC_{50}, Fish or Invertebrate	<1 mg/l	NIOSH, 1976
Longevity Factor (Soil Life Persistence)	>5 wks	Weber, 1977
Bioaccumulation (highly accumulative)	$>8000 \frac{\text{tissue conc.}}{\text{water conc.}}$	Weber, 1977

If toxicological data are available in one of these categories, it can be compared to the threshold levels for extreme toxicity. Although unregulated, a substance revealed by this method to be extremely toxic or hazardous deserves serious consideration for monitoring to link source emissions to potential health or ecological effects. For a less toxic substance, a more refined approach is needed to be able to select, with confidence, whether it should be monitored in the ambient environment.

PAGE NUMBER
EPA Form 2350-4 (4-80)
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This simplified screening process is most useful when the contribution of the FBC process to ambient levels of a pollutant is unknown, and should be replaced by a more sophisticated priority ranking procedure (discussed in the following sections) when site/facility data become available.

Summary of the Categorization Process

The result of completing the first phase of the selection procedure is a grouping of effluent components by categories. Category I pollutants are to be monitored to meet the standards and regulations addressing operation of FBC processes and gather information on unregulated pollutants strongly suspected of having the potential to impact public health and ecological systems. Category II pollutants are monitored in anticipation of federal requirements for compliance. Category III pollutants are unregulated substances for which there is either only limited effects information or evidence of only slight-to-moderate hazard to potential receptors. The need to monitor substances in Categories II and III is based primarily on the monitoring objectives of the program. It is assumed that these objectives recognize the need to support health and ecological research programs. The primary criterion for selecting a substance in Categories II and III for the monitoring program is the likelihood that the substance would pose a problem if it were to enter the ambient environment. This is determined in the second phase of the selection procedure, which identifies an effects threshold level and an estimate of potential hazard for substances not previously assigned a legal criterion. Also in this phase, the substances in the three categories may be readjusted, e.g., if health or ecological studies suggest that a legal standard or criterion for a pollutant should be changed, a new effects threshold level can be derived for the substance and it can be processed further as a Category III substance.

PRIORITY RANKING

Overview

Priority ranking is a procedure developed to select from the unregulated pollutants produced by a source those substances which should be monitored in the ambient environment. Since priority ranking estimates the potential damage to health or the environment from expected emissions generated by the source, it addresses monitoring objectives to link source to effects. The procedure consists of two major activities.

The first, estimating the potential for receptor damage for each unregulated pollutant generally requires at least two data elements--a factor representing known damage effects of the substance and the amount or rate of production of the substance by the source. In the absence of actual data, values for either of these elements should be assumed or estimated for a specific FBC source. The second activity combines the two factors derived in the first step as a simple ratio or more complex algorithm to formulate a hazard index. A decision rule is then developed that serves as a basis for completing a preliminary list of Category III pollutants that need to be monitored according to information contained in the hazard indices.

Identification of the Potential for Receptor Damage from Unregulated Pollutants

The primary criterion for evaluating the damage potential of an unregulated pollutant is either a suspected health or ecological effect. Other effects, on non-living materials for instance, can also be considered. In any case, information sources on effects of each of the unregulated pollutants are reviewed and the available data are translated into a threshold concentration, derived from the concentrations known to produce effects on receptors. Ideally, a minimum effects threshold concentration can be estimated, the receptor exposure concentration below which effects should not be observed. If appropriate data are available, this should be estimated for critical or sensitive receptors in the environment (children, hypersensitive individuals, endangered species, etc.)

The minimum effects threshold level concentration serves as a scaling factor or index of the minimum potential hazard, reflecting the maximum acceptable environmental concentration of the substance that is unlikely to cause serious acute or chronic health or ecological effects. This minimum threshold concentration is analogous to a standard or criterion. Since this concentration is estimated by one of many available procedures, the error associated with the estimate should also be calculated to determine to what degree the threshold is likely to be exceeded.

Assigning minimum hazard indices requires an extensive understanding of the methods (and pitfalls) associated with utilizing toxicological and ecological effects data on a suspected pollutant (Cairns and Maki, 1979; Draggan and Giddings, 1978).

Most variations in the derivations can be traced to quantification of value judgments concerning relative environmental impact or potential for causing damage to receptors in the absence of primary data (Jones, 1978).

Representative systems were reviewed and evaluated for determining potential minimum hazard levels for pollutants. Implementation of the selection procedure should begin with a review of all available systems before selecting the most appropriate procedure consistent with the objectives of the monitoring plan.

The EPA has recently funded a program to identify minimal effects concentrations for pollutants generated by fossil fuel combustion and conversion processes (Cleland and Kingsbury, 1977; Kingsbury and White, 1979). This system, the Multimedia Environmental Goals (MEGs), was developed by several support contractors for the EPA. Because it is undergoing continued refinement within the EPA, it was given the greatest attention in this review.

MEGs are concentration-level goals for hundreds of trace contaminants found in the effluents of coal and oil conversion processes (Cleland and Kingsbury, 1977). MEGs have been derived for pollutants based on both health and ecological effects and are tabulated for the air, water, and land media. Currently, MEG values are available for many of 650 substances in the original publication (Cleland and Kingsbury, 1977; Kingsbury and Sims, 1978); MEGs are updated periodically for various organic and inorganic compounds.

The initial intent of establishing MEG values for chemical substances was to provide scaling factors to 1) provide decision criteria in assessing the impact of a source on the environment, 2) use in systems to establish priorities among pollutants considered for possible regulation, and 3) influence developments in control technology. These reports collate diverse data sets in a coherent, efficient fashion and explore related subjects.

One major category of MEGs is Minimum Acute Toxicity Effluents (MATEs). MATE values are approximate concentrations of contaminants in undiluted source emissions to air, water, or land which probably will not immediately evoke harmful or irreversible responses in exposed humans or other organisms, when those exposures are limited to short periods of time (Table 28). Figure 22 shows how MATEs are derived for each medium.

The second major category of MEGs is Estimated Permissible Concentrations (EPCs). These are concentration levels in the ambient environment that are considered to be safe for continuous exposure. Twenty-two different kinds of EPCs are defined, with some EPCs secondarily derived from other EPCs. In the event that multiple data exist for a substance, only the lowest EPC for a given medium is reported.

TABLE 28. EMISSION LEVEL GOALS FOUNDATIONS
(Cleland and Kingsbury, 1977)

	EMISSION LEVEL GOALS						
	I. BASED ON BEST TECHNOLOGY		II. BASED ON AMBIENT FACTORS				
	A. Existing Standards	B. Developing Technology	A. Minimum Acute Toxicity Effluent		B. Ambient Level Goal		C. Elimination of Discharge
	NSPS, BPT, BAT	Engineering Estimates (R&D Goals)	Health Effects	Ecological Effects	Health Effects	Ecological Effects	Natural Background
Air	Methodology not yet developed	Methodology not yet developed	Foundation: $^{o}\mathrm{MATE}_{AHS}$ $^{o}\mathrm{MATE}_{AH1(a)}$ $^{o}\mathrm{MATE}_{AH2}$ $^{o}\mathrm{MATE}_{AH3}$ $^{o}\mathrm{MATE}_{AC1}$ $^{o}\mathrm{MATE}_{AC2}$	Foundation: $^{o}\mathrm{MATE}_{AE}$	Foundation: $^{o}\mathrm{EPC}_{AHS}$ $^{o}\mathrm{EPC}_{AH1}$ $^{o}\mathrm{EPC}_{AH3}$ $^{o}\mathrm{EPC}_{AC1}$ $^{o}\mathrm{EPC}_{AC2}$ $^{o}\mathrm{EPC}_{AT}$	Foundation: $^{o}\mathrm{EPC}_{AE}$	Foundation: ^{o}Rural background concentrations
Water			Foundation: $^{o}\mathrm{MATE}_{WHS}$ $^{o}\mathrm{MATE}_{WH1}$ $^{o}\mathrm{MATE}_{WC}$	Foundation: $^{o}\mathrm{MATE}_{WES}$ $^{o}\mathrm{MATE}_{WE1}$	Foundation: $^{o}\mathrm{EPC}_{WHS}$ $^{o}\mathrm{EPC}_{WC}$ $^{o}\mathrm{EPC}_{WC}$ $^{o}\mathrm{EPC}_{WT}$	Foundation: $^{o}\mathrm{EPC}_{WE1}$ $^{o}\mathrm{EPC}_{WE2}$	Foundation: ^{o}Natural concentrations in surface waters ^{o}Concentrations measured in drinking water ^{o}Natural seawater concentrations
Land			Foundation: $^{o}\mathrm{MATE}_{LH1}$	Foundation: $^{o}\mathrm{MATE}_{LE1}$	Foundation: $^{o}\mathrm{EPC}_{LH}$ $^{o}\mathrm{EPC}_{LC}$ $^{o}\mathrm{EPC}_{LT}$	Foundation: $^{o}\mathrm{EPC}_{LE}$	Foundation: ^{o}Typical soil concentrations

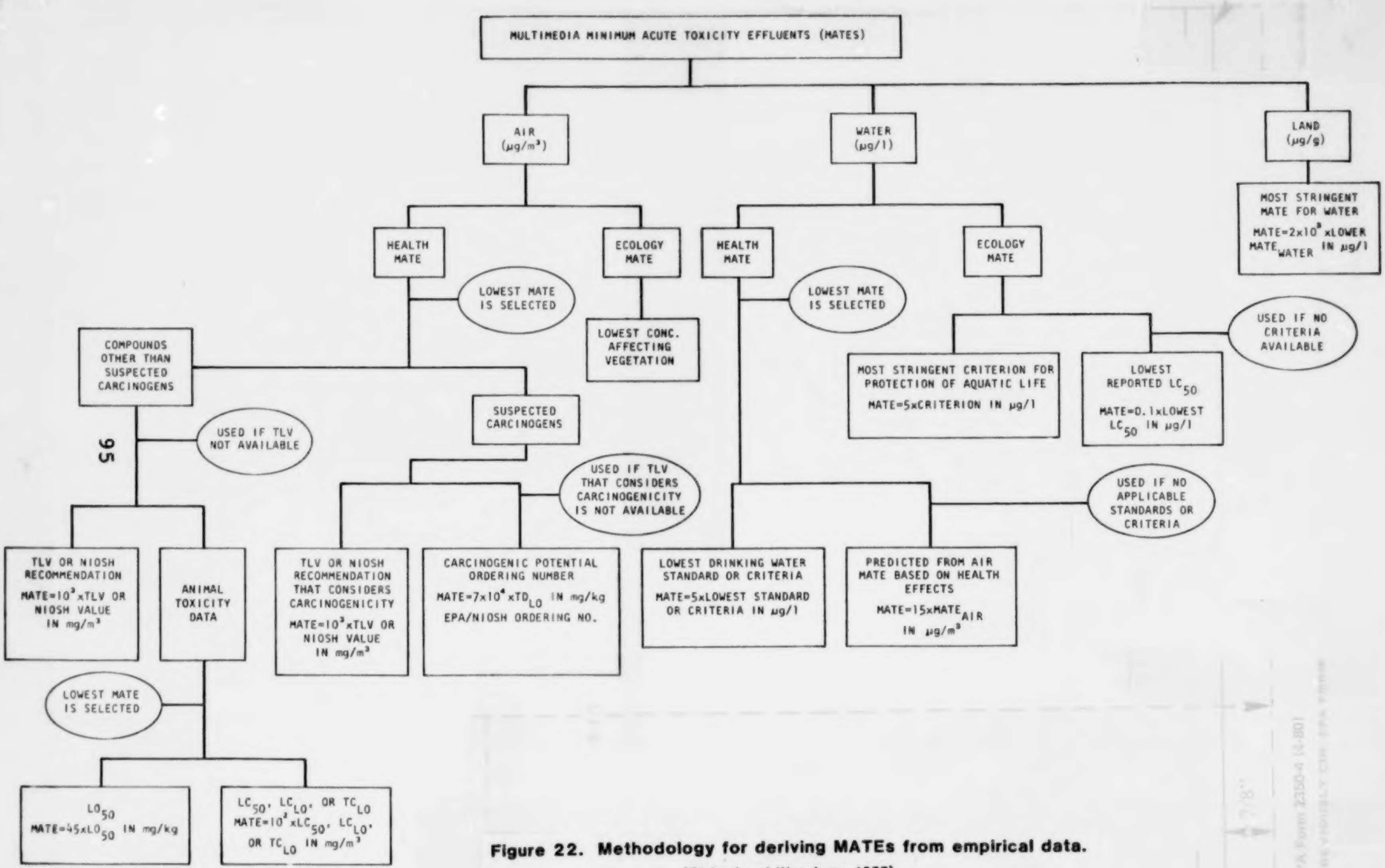
MULTIMEDIA MINIMUM ACUTE TOXICITY EFFLUENTS (MATES)
AIR ($\mu g/m^3$)
WATER ($\mu g/l$)
LAND ($\mu g/g$)
HEALTH MATE
ECOLOGY MATE
HEALTH MATE
ECOLOGY MATE
MOST STRINGENT MATE FOR WATER $MATE=2\times10^3\times LOWER\ MATE_{WATER}$ IN $\mu g/l$
LOWEST MATE IS SELECTED
LOWEST CONC. AFFECTING VEGETATION
LOWEST MATE IS SELECTED
USED IF NO CRITERIA AVAILABLE
COMPOUNDS OTHER THAN SUSPECTED CARCINOGENS
MOST STRINGENT CRITERION FOR PROTECTION OF AQUATIC LIFE $MATE=5\times CRITERION$ IN $\mu g/l$
LOWEST REPORTED LC_{50} $MATE=0.1\times LOWEST\ LC_{50}$ IN $\mu g/l$
SUSPECTED CARCINOGENS
USED IF TLV NOT AVAILABLE
USED IF TLV THAT CONSIDERS CARCINOGENICITY IS NOT AVAILABLE
USED IF NO APPLICABLE STANDARDS OR CRITERIA
TLV OR NIOSH RECOMMENDATION $MATE=10^3\times TLV$ OR NIOSH VALUE IN mg/m^3
ANIMAL TOXICITY DATA
TLV OR NIOSH RECOMMENDATION THAT CONSIDERS CARCINOGENICITY $MATE=10^3\times TLV$ OR NIOSH VALUE IN mg/m^3
CARCINOGENIC POTENTIAL ORDERING NUMBER $MATE=7\times10^4\times TD_{LO}$ IN mg/kg EPA/NIOSH ORDERING NO.
LOWEST DRINKING WATER STANDARD OR CRITERIA $MATE=5\times LOWEST$ STANDARD OR CRITERIA IN $\mu g/l$
PREDICTED FROM AIR MATE BASED ON HEALTH EFFECTS $MATE=15\times MATE_{AIR}$ IN $\mu g/m^3$
LOWEST MATE IS SELECTED
LD_{50} $MATE=45\times LD_{50}$ IN mg/kg
LC_{50}, LC_{LO}, OR TC_{LO} $MATE=10^2\times LC_{50}$, LC_{LO}, OR TC_{LO} IN mg/m^3

Figure 22. Methodology for deriving MATEs from empirical data.

(Cleland and Kingsbury, 1977)

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TABLE 29. BASIC DATA AND DERIVATIONS FOR AMBIENT LEVEL GOALS
(Cleland and Kingsbury, 1977)

	AMBIENT LEVEL GOALS				
	I. Current or Proposed Ambient Standard or Criteria		II. Toxicity Based Estimated Permissible Concentrations		III. Zero Threshold Pollutants Estimated Permissible Concentrations
	A. Health Effects	B. Ecological Effects	A. Health Effects	B. Ecological Effects	Health Effects
Air	Basic Data: °Primary Ambient Air Quality Standard (existing or proposed) °Criteria for Hazardous Air Pollutant Emission Standards	Basic Data: °Secondary Ambient Air Quality Standard (existing or proposed)	Basic Data: °TLV °NIOSH Recommendation °LD_{50} (or substitute)	Basic Data: °Lowest concentration affecting sensitive vegetation (24 hrs)	Basic Data: °TLV (oncogenicity) °NIOSH Recommendation (oncogenicity) °Adjusted Ordering Number (species, route of administration, lowest effective dosage as carcinogen or as teratogen)
	Derivation: °Basic Data (EPC_{AHS})	Derivation: °Basic Data	Derivation: °$EPC_{AH1(a)}$ °EPC_{AH3}	Derivation: °EPC_{AE}	Derivation: °EPC_{AC1} °EPC_{AC2} °EPC_{AT}
Water	Basic Data: °Drinking Water Regulation or Criteria	Basic Data: °Water Quality Criteria Established for Protection of Aquatic Life	Basic Data °TLV °LD_{50} (or substitute)	Basic Data: °Lowest Aquatic LC_{50} and Application Factor °Tainting Level °Application Factor or Hazard Level from Water Quality Criteria °Accumulation Factor and Allowable Flesh Concentration	Basic Data: °$EPC_{AC(1,2)}$ °EPC_{AT}
	Derivation: °Lowest Value from Basic Data (EPC_{WHS})	Derivation: °Lowest value from Basic Data (EPC_{WES})	Derivation: °EPC_{WH2}	Derivation: °EPC_{WE1} °EPC_{WE2} °EPC_{WE3} °EPC_{WE4}	Derivation: °EPC_{WC} °EPC_{WT}
Land	Basic Data: °None Available (in appropriate units)	Basic Data: °None available	Basic Data: °$EPC_{WH(S2)}$	Basic Data: °$EPC_{WE(S,1,2,3,4)}$	Basic Data: °EPC_{WC} °EPC_{WT}
	Derivation: °None	Derivation: °None	Derivation: °EPC_{LH}	Derivation: °EPC_{LE}	Derivation: °EPC_{LC} °EPC_{LT}

EPCs and MATEs are based on data of diverse origins (Table 29). Currently available EPCs and MATEs are based on threshold limit values (TLVs), current and proposed ambient standards, criteria, regulations, and recommendations; toxicity, carcinogenicity, mutagenicity, and teratogenicity data; and nuisance factors. Additional MATEs are expected to be developed from data on technological factors in the future (Kingsbury, G.L., EPA, to Kangas, M.J., personal communication).

To keep the MEG values conservative, simplified "worst case" assumptions were made in deriving algorithms for specific EPCs and MATEs. In general, MATE values for a substance are higher than the corresponding EPC value, and both values are higher than the reported natural background concentrations.

A standard nomenclature is used to identify MATEs and EPCs that indicate the media and type of effect addressed, data used to derive MEG value, and model number. The subscripts and their meaning are:

A	Air
W	Water
L	Land
H	Health effect
E	Ecological effect
C	Carcinogenicity
T	Teratogenicity
S	Standard or criteria
1-4	Reference to specific models or algorithms
a	MEG expressed in ppm instead of micrograms/ per liter, gram, or cubic meter

In this discussion, it is assumed that the MEGs are used primarily in the EPA project as scaling factors for ranking pollutants or emission streams for a source-oriented ambient monitoring program. Furthermore, this preliminary evaluation does not include a comparison of MEGs to other similar scaling factors or priority ranking systems. Disadvantages associated with the MEGs include the following:

- The MEG methodology does not consider synergisms, antagonisms, or other secondary pollutant associations.
- Significant data gaps exist in MEGs for land, which are based on simplified assumptions and air and

water data. Modifications to the models for deriving land MEGs were adopted in February 1978, to overcome the overly conservative aspects of the end values published in the original volume (Kingsbury, G.L., EPA, to Kangas, M.J., personal communication).

- Human health effects are extrapolated from animal toxicity data. Models and assumptions frequently include arbitrary factors or constants, e.g., safety factors used to translate animal LD_{50} data to human health effects.
- Inappropriate use of MEGs as a substitute for standards, criteria, or recommendations is possible, if they are not recognized as being only preliminary scaling factors.
- No explicit provision is made for error estimates or confidence intervals associated with MEG values.
- MEGs are meaningful for primary pollution effects only. If any changes in the chemical nature of a substance occur in the effluent stream or ambient environment, a different MEG value would have to be referenced.
- The overall level of confidence associated with any MEG is no greater than the health effects or toxicity data used in the particular model. All standard criticisms applied to these data (inadequate or unspecified sample size, conditions under which the data were obtained, etc.) apply also to the MEGs.
- Safety factor for MATEs is less than that for EPCs, on a proportional basis, e.g., if an EPC is exceeded by some fraction (%), the actual impact may be much less than if a MATE were exceeded by the same fraction (%).
- Non-exceedance of a MATE may be mistaken to mean that effluents do not have the potential of creating problems in the ambient environment. However, MATEs = TLVs for many substances, and effects can occur below TLVs on some sensitive receivers. TLVs are for healthy workers, not for the more sensitive members of the general public.
- MATEs for presumptive or suspected carcinogens do not accommodate factors involving synergisms, co carcinogenicity, promotion, and metabolic alterations into more or less active metabolites.
- Certain application factors used in MATE models have been selected subjectively.
- Values for solid waste (land) MATEs are simply scaled from water MATEs, and some water MATEs are scaled from air MATEs.
- Some EPCs for land and water are secondarily based

on health effects and animal toxicity data. Introduction of additional arbitrary factors and constants has the potential of compounding or magnifying error in derived values, e.g., EPC_{WH1} based on EPC_{AH}; EPC_{LH} based on EPC_{WH}.

- "Land" MEGs are scaled from water MEGs, which are more likely to reflect biological effects since impacts of pollutants in solution are probably more serious than those generated by "dry" material.

Advantages associated with the MEGs include the following:

- MEGs are readily available for many chemical substances likely to be components of effluents from facilities utilizing advanced fossil fuel combustion and conversion processes.
- The MEG methodology is currently being extended to non -chemical degradants.
- Algorithms for deriving MEG values are designed to address health and ecological effects in all media, based on a wide variety of data. Data used to derive published MEG values have been priority ranked to use best available information (standards and criteria, epidemiological data, TLVs and NIOSH recommendations before animal toxicity data; LD_{50}[oral, rat] before other toxicity data, etc.)
- MEGs for Zero Threshold Pollutants (carcinogens, teratogens, and mutagens) are published for all media and consider such factors as animal test species, recorded human effects, etc.
- Phytotoxicity, reported tainting levels, bioaccumulation and potential biomagnification data are incorporated in deriving MEGs when available.
- When several data sets are available for a substance, each is used to calculate a MEG value, but only the most stringent value is reported.
- Further development and extensions of the MEG methodology is in progress. The existing system is designed to use new information as it becomes available, without modifying models, although new models may eventually be developed.
- MEGs are designed for direct use in Source Assessment Models (SAMs).
- Selection of substances for MEGs emphasizes many of the contaminants and degradants expected in FBC effluents.
- In the event that the MEG methodology is not utilized, the background information summarized in the MEG charts is useful in priority ranking, selection of sampling and analysis methods, and Level 1, 2, or 3 source analysis.

The MEG background information summaries are a significant collection of data on chemical substances that could be expected in the emissions from FBC processes. In the event that a system of priority ranking of pollutants other than the MEG/SAM model system is selected, the data in these summaries may be directly applicable in the alternative system selected.

An alternative approach that has some similarity to the MEGs developed as a response to assessing applications for permits for new or modified air pollution sources submitted to the Texas Air Control Board (Price et al., 1979). The bases for decisions associated with their permit review process were ambient levels called Acceptable Public Exposure Levels (APEL) derived from existing toxicological data to indicate acceptable levels for short duration exposure. These levels were derived by applying a reduction factor for healthy adult males to available occupational health or toxicity data on each substance. A reduction of 0.03 is used when only slight-to moderate effects are indicated and available toxicity data indicate none of the following acute effects: irritation from short-term exposure, sensitization, "relatively severe effects," or an occupational ceiling limit and exposure. Otherwise, a factor of 0.01 is used. The data bases reviewed for each substance include TLVs (ACGH), OSHA standards, NIOSH recommended levels, and available oncogenic and genotoxic information. Currently, the authors are compiling a list of APELs, which could be used for priority ranking pollutants produced in the effluents of FBC processes.

The main advantage of this approach is, however, that it uses health effects data and compiles the original data and comments into a clearly formatted list; its major drawback is the subjective assignment of a reduction factor to be applied to original health effects data to determine the APEL.

Walsh et al. (1978) derive a threshold effects concentration which is used to define a hazard index for assessing limited exposures to environmental pollutants. The threshold concentration (Q_L) is a value selected to establish a limit for humans which should not be exceeded because of health risks. Stated in terms of total-body, organ, or tissue burden, Q_L involves identifying a human health endpoint such as a statutory limit, standard organ level, total-body burden, or specific disease state.

A second study applied this approach to cadmium release from a smelter operation in Helena, Montana (Rupp et al., 1978). The critical human health endpoint selected for the test of the procedure uses the kidney cortex, based on a review of cadmium toxicity. Therefore, 200 mg Cd/g was the value selected for Q_L. Utilizing human organ effects to establish an ambient level goal may not always be possible, due to the lack of effects data for many organic pollutants and less toxic organics. In calculating Q_L, however, a thorough consideration is given to the physiological properties of the receptor, chronic exposure, and tissue bioaccumulation. While too detailed as a preliminary screening process, this approach could be valuable once a specific facility utilizing the FBC process, site factors, and receptor populations have been identified.

A number of systems utilize a rank order number to indicate potential receptor damage (Ingraham and Zechel, 1979; Jones, 1978; TSCA Interagency Committee, 1977).

Ingraham and Zechel (1979) develop a hazard index for a substance based on expected impacts on an individual human receptor, incorporating this value into a simple model to indicate the potential hazard a particular source presents to the population in nearby areas. This approach could potentially be utilized for sensitive ecological receptors.

The hazard is a percentage rank estimated subjectively from a review of medical reports of damage. Four percentage categories were used by the authors in comparing the relative receptor damage from lead and cadmium: 25, 50, 75 and 100. In this case, lead was assigned value of 50 and cadmium a value of 100, since medical reports indicated cadmium damage to humans is considerably more severe than that of lead.

This approach has several disadvantages. If a large number of substances have to be considered, assigning relative percentages would become almost impossible. The manner in which relative degree of hazard to receptors is estimated from a review of the relevant literature is not given by the authors. Finally, an index based on actual data on the damage to potential receptors would be more desirable; it would represent a level which could be compared to an expected emission rate or an environmental concentration.

Some of the systems used for deriving threshold concentrations for single pollutants are summarized in Table 30. The approaches estimating values for effects threshold concentrations utilize available information more effectively than systems deriving a single rank value to indicate potential hazard to receptors.

Identification of Emission Rates and Ambient Level Concentrations

The second data elements needed for priority ranking are emission rates or ambient level concentrations for each unregulated pollutant. Threshold levels for potential effects

TABLE 30. APPROACHES TO ESTIMATING AMBIENT LEVEL GOALS (ALG) WHICH FUNCTION AS MINIMUM POTENTIAL HAZARD LEVELS IN THE AMBIENT ENVIRONMENT

Reference	Method of deriving an ambient level goal
Cleland and Kingsbury, 1977 Kingsbury and White, 1979	Simple models are applied to all relevant health and ecological hazard data
Price et al., 1979	Simple reduction constants are applied to all relevant health hazard data
Walsh et al., 1978 Rupp et al., 1978	Total exposure burden/dose limit is calculated for human receptor organ most sensitive to pollutant.
Ingraham and Zechel, 1979	Simple relative rank order value (a percentage) is subjectively assigned to all pollutants considered based on a literature review of known health effects.

can be adjusted by a factor representing production expected from the source. It is assumed that this parameter is estimated during the analysis of the FBC process that occurs at the beginning of the monitoring design procedure. Otherwise, emission rates or environmental concentrations must be assumed from a hypothetical scenario. In principle, as data on effluents from many demonstration level FBC facilities become available, scaling factors can be derived to project emission rates of specific pollutants from commercial-scale plants.

In addition to estimating potential ambient concentrations for each pollutant addressed during priority ranking, careful consideration of the emission rate expected from the FBC process with respect to background ambient levels is required. If expected emission rates are significantly below ambient background levels, serious problems of measurement may result. This effect must be taken into account in deciding whether monitoring this pollutant will be technically feasible.

Three basic approaches were identified in a review of the literature on priority ranking substances based on their potential for causing environmental effects. (They are summarized, with appropriate references, in Table 31.) Each approach is reviewed briefly in the following paragraphs.

TABLE 31. APPROACHES TO ESTIMATING AMBIENT ENVIRONMENTAL CONCENTRATIONS EXPECTED TO IMPACT HUMAN AND ENVIRONMENTAL RECEPTORS

Reference	Method of deriving expected ambient concentrations
Walsh et al., 1978 Behar et al, 1979 Rupp et al., 1978	Authors use site-specific atmospheric, terrestrial and aquatic transport models to estimate human exposure and physiological transport models to estimate organ exposure concentrations
Anderson et al., 1978 Eimutis, 1976 Reznik et al., 1978	Ambient level concentrations are estimated by simple dispersion models for gaseous, liquid and solid discharges from fossil fuel combustion and conversion facilities.
Berkowitz et al. (In Jones, 1978) TSCA Interagency Testing Committee, 1977	"Two reservoir" model is used to evaluate the rate of entry of water pollutants to the aqueous environment.

Behar et al. (1979) present the conceptual framework for modeling the flow of a quantity of a pollutant through all environmental media once it leaves a source, but give no specific mathematical models. Walsh et al. (1978) provide specific mathematical formulations utilizing a similar approach.

The models proposed by Walsh et al. are implemented for cadmium transport by Rupp et al., 1978. Walsh et al. offer the most detailed approach available, one which has the potential for most closely estimating the actual concentrations of a substance which may impact a specific receptor. Two serious problems, however, are that models cannot be simplified to accommodate missing data; and that the models, in their present form, do not allow probability statements to accompany estimates of exposure concentration.

Anderson et al. (1978), Eimutis (1976), and Reznik et al. (1978) also use a multimedia approach but employ simpler modeling methods to estimate quantities of a pollutant generated by a source. These simpler approaches are valuable when information availability is low.

An example of the many other studies relevant to tracing environmental concentrations is the approach developed by Berkowitz et al. (Jones, 1978), which should be reviewed for modeling ambient environmental concentrations of a pollutant in aquatic environments. Dispersion models for predicting movement of airborne pollutants could also be used to estimate potential exposure concentrations when appropriate emission data are available.

Methods of Combining Effects and Concentration Values to Estimate Hazard Potential

A method of combining appropriate data on potential effects and expected ambient concentrations is desirable for estimating the hazard potential of each pollutant. Where rank values indicate potential effects and ambient concentrations, various weighting algorithms are used to estimate potential hazard (Jones, 1978; TSCA Interagency Testing Committee, 1977). When expected concentrations are used directly, some form of ratio of the expected environmental concentration or emission rate to potential effects concentration is used to indicate potential damage to receptors (Petrie and Kingsbury, 1978; Reznik et al., 1978; Walsh et al., 1978; Rupp et al., 1978).

A method utilizing assigned rank values was developed by the TSCA Interagency Testing Committee to select substances which should be added to the inventory list of substances required under Section 4(e) of the Toxic Substances Control Act (TSCA), Public Law 94-469. The approach rank orders chemicals for priority in testing to determine their effects on human health and the environment. The initial priority of the j^{th} chemical is given by the equation:

$$rj = \sum_{i=1}^{4} w_i \frac{f_{ij}}{s_i} \qquad (17)$$

Where:

w_i = weight assigned to the i^{th} factor
f_{ij} = the i^{th} factor score for the j^{th} chemical
s_i = a scaling factor chosen to normalize the factor scores.

The following factors were considered:

- Annual national production of the chemical
- Environmental burden of the chemical in terms of:
  - The quantity released into the environment nationwide
  - The persistence of the chemical
- Occupational exposure
- Extent to which the general population is exposed, which involves four subfactors:
  - Number of people exposed
  - Frequency of exposure
  - Intensity of exposure
  - Penetrability (i.e., ability of the chemical to enter the body)

The chemicals that scored high were further evaluated by the method described below (unless they were eliminated for another reason, e.g., already a regulated substance). Eight factors were considered with each factor having a possible numerical value of from 0 to 3. The values for the eight factors are then summed to obtain the priority value for the chemical in question. The factors are:

- Carcinogenicity
- Mutagenicity
- Teratogenicity
- Acute toxicity
- Other toxic effects
- Bioaccumulation

- Ecological effects (includes toxic effects on non-human organisms and effects on ecosystems, atmosphere, and climate)

- Hazardous contaminants and environmental degradation or conversion products

The TSCA scheme is not entirely appropriate. First, it includes factors to evaluate a chemical's annual national production by chemical manufacturers and its release by all users of the chemical. While this is essential to TSCA, it is inappropriate for selecting pollutants for ambient monitoring of an FBC process. Second, the ecological factors considered do not include site-specific considerations, such as the evaluation of probable effects on socially valuable species in the immediate vicinity of the plant.

An example of the second approach to estimating hazard potential are the Source Assessment Models (SAMs) developed for the EPA. At least two SAMs, developed by Acurex Corporation, are currently under consideration by the EPA: SAM 1 and SAM 1A. Although still in draft form, SAM 1 can be used to illustrate the approach. This model considers peak ambient concentrations and derived emission level goals based on goals for peak allowable ambient concentrations (EPCs) (Anderson et al., 1978). The model proposed for SAM 1 defines the degree of hazard for a pollutant species as:

$$H_f = \begin{matrix}\text{Pollutant}\\ \text{Species}\\ \text{Degree of}\\ \text{Hazard}\end{matrix} = \frac{C}{K\ ALG_m} = \frac{\text{Discharge Pollutant Concentration}}{\text{Discharge Level Goal}} \quad (18)$$

Discharge level goal = Emission level goal = $K\ ALG_m$

Where

$$K = \begin{matrix}\text{dispersion or}\\ \text{dilution factor}\end{matrix} = \begin{matrix}\text{Source Stream}\\ \text{Dilution Factor}\end{matrix} = \frac{C}{X}$$

C = Discharge level concentration
X = Ambient concentration

ALG = Ambient level goal (e.g., an EPC)
ALG_m = Smallest of EPC values

The SAM 1A model priority ranks pollutants according to the ratio of the total emission rate for an individual chemical from all air or water pollution sources at a facility, divided by the MATE value for the chemical (Schalit and Wolfe, 1978). Priority ranking based on the SAM 1A system is independent of the resulting ambient concentration. It assigns the same relative priority to an emission of 5 grams per second of beryllium if it were emitted 200 meters above the ground or at ground level, regardless of the fact that the ground level emission would cause higher ambient concentration. This system tends to consider the total burden of a pollutant in the environment and how widespread the impact.

Under SAM 1A, pollutants would be assigned higher priorities according to increasing values of the toxic unit discharge rate for the pollutant (TP_i, where i identifies the pollutant):

$$TP_i = \sum_{k}^{n} H_{ik} Q_k = \sum_{k}^{n} \frac{C_{ik}}{MATE_{ik}} \bullet Q_k \qquad (19)$$

Where

i = pollutant

k = effluent stream

n = number of effluent streams

C_{ik} = concentration i'th pollutant in k'th effluent stream

$MATE_{ik}$ = MATE value for i'th pollutant in the medium corresponding to k (8 hour MEG goal)

Q_k = volume rate of flow in effluent stream k

$H_{ik} = \frac{C_{ik}}{MATE}$ = Hazard factor i'th pollutant, k'th stream

This procedure would be performed separately for those MATEs based on ecological effects and those based on health effects, in order to priority rank each separately, according to effects. If a priority ranking based on both types of effects is desired, the smaller of the MATEs (based on health versus ecological effects) could be used.

In principle, pollutants in air and water effluents could be priority ranked together by adding the TP_i's in air and in water. This might be useful for multimedia health-related monitoring programs--similar to the type of program in the EPA Las Vegas Integrated Exposure Assessment Monitoring Program (Behar et al., 1979). It is also possible to priority rank in terms of a MATE based on carcinogenicity only, toxicity only, or any other basis for which separate MATE values have been calculated.

A distinct advantage of SAM 1A is that it is currently being applied to effluent data from fluidized bed boilers and from coal gasification plants by EPA contractors. Priority ranked lists of pollutants using this system are available for some pilot-scale facilities (Anderson et al., 1978; Murthy et al., 1977; Murthy and Henschel, 1978).

The SAM models have an important limitation. The degree of hazard estimated by a SAM model is influenced by a MEG value. If the MEG value is known to be invalid, the estimated hazard potential is also questionable. Likewise, the hazard index of a substance estimated by any other procedure could be questioned if evidence indicates that available data underestimate potential effects or ambient concentrations. SAMs and MEGs are meant only as a "first iteration" priority ranking system, a mechanism to make an intelligent guess on what should be monitored, what is hazardous and what is not, and the relative degrees of hazard.

DEVELOPMENT OF A DECISION RULE TO SELECT POLLUTANTS FOR MONITORING BASED ON THEIR POTENTIAL FOR ENVIRONMENTAL HAZARD

Two approaches were considered to decide whether a pollutant should be considered further for monitoring, the principal assumption being the existence of a hazard index incorporating effects and expected concentrations or emission rates. The first approach considers each pollutant independent of all other pollutants generated by a source. If the expected emission rate or environmental concentration exceeds the estimated minimum effects threshold concentration or emission rate, the substance is considered further for monitoring.

An alternative approach involves ranking all pollutants by hazard index value and considering the pollutants having the largest hazard values for monitoring. The group of Category III pollutants can be handled as a population or sample, and appropriate statistical parameters of the array selected as possible cutoff points for the decision to monitor. The median, for example, would segregate the array symmetrically, with half the pollutants ranking above the median and half below. Instead of using a statistical parameter as a cutoff point in the array as a decision criterion, "orders of magnitude" values could be selected (e.g., greater than 1, between 1 and 0.1, between 0.1 and 0.01).

These alternatives offer objective ways of selecting a pollutant for monitoring when no clear criteria are available. Other alternatives are possible, and may in fact address monitoring objectives more effectively. Whatever system is selected, professional judgment must be balanced with explicit rules or guiding principles in selecting unregulated pollutants for monitoring.

PREPARATION OF THE PRELIMINARY LIST OF POLLUTANTS TO BE MONITORED

After categorizing and priority ranking of all pollutants are completed, all support parameters required to interpret Category I, Category II, or potentially hazardous Category III pollutants are identified. A combined listing of all of these substances and parameters is compiled as a basis for further refinement in the selection process. At this next level of analysis, availability, cost-effectiveness, accuracy, and quality assurance requirements of sampling and analytic methods for each substance and its support parameters are considered. This final phase of the selection process is presented in the next section.

FINAL SELECTION OF POLLUTANTS BASED ON TECHNICAL AND COST CONSIDERATIONS

The first phase of this priority ranking scheme has developed an outline for 1) chemically characterizing source effluents, 2) identifying potential health and ecological problems associated with potential pollutants, and 3) establishing the potential for exceedance of existing or proposed standards or other threshold criteria. These determinations were used to select a preliminary list of pollutants for monitoring. This section extends the priority ranking procedure to evaluate the need for source-oriented ambient monitoring with respect to cost and technical problems and alternative approaches to monitoring sources.

The first part of the priority ranking scheme allowed one of the following conclusions:

- Insufficient data are available to determine with any degree of confidence that one or more substances need to be monitored,

- Sufficient data are available to show that one or more substances do not require monitoring, or

- Sufficient data are available to support a decision that a substance needs to be monitored.

An action plan to support the first conclusion would begin by exploring appropriate procedures for effluent characterization. Any monitoring other than that required for construction permits would be delayed until an evaluation of the facility's emissions is completed.

The second conclusion, with regard to specific substances in source effluents, requires no continuous monitoring of the FBC process. Periodic source checks are valuable, however, to detect an increase in these substances to problem levels. A standard plan to monitor during unanticipated process upsets could also be developed under this conclusion.

If the analysis used in the priority ranking procedure suggests that a substance should be monitored, an appropriate action plan could be developed only after additional analysis is completed. This additional analysis is the subject of the following discussion.

Technical Quality of Available Analytical Methods

It is assumed that a preliminary sampling plan has been developed which specifies the frequency, location, and intensity of sampling for each problem pollutant produced by the facility. This information is required to specify the analytical methods appropriate for the monitoring program.

Technical quality of available analytic methods must be considered as part of the selection process. For many pollutants, if an EPA-approved method is applicable in the situation being considered, this will eliminate the need for further consideration of other technical methods. However, care must be taken to ensure that the approved method is indeed applicable (e.g., no interferences, equipment available for required sampling locations and frequencies), before the resultant cost can be estimated for the overall monitoring program. The following text, with reference to Figure 23, presents the technical aspects in detail.

As shown in Figure 23, the pollutants and parameters considered for monitoring are divided into two groups: chemical pollutants and physical and support parameters. The major portion of the following discussion focuses on method selection procedures for chemical pollutants.

Chemical pollutants for which EPA-approved methods are indicated by regulations, permit conditions, or program objectives (Step 2) must be considered, together with anticipated concentrations of interfering co-pollutants (Step 3). If a

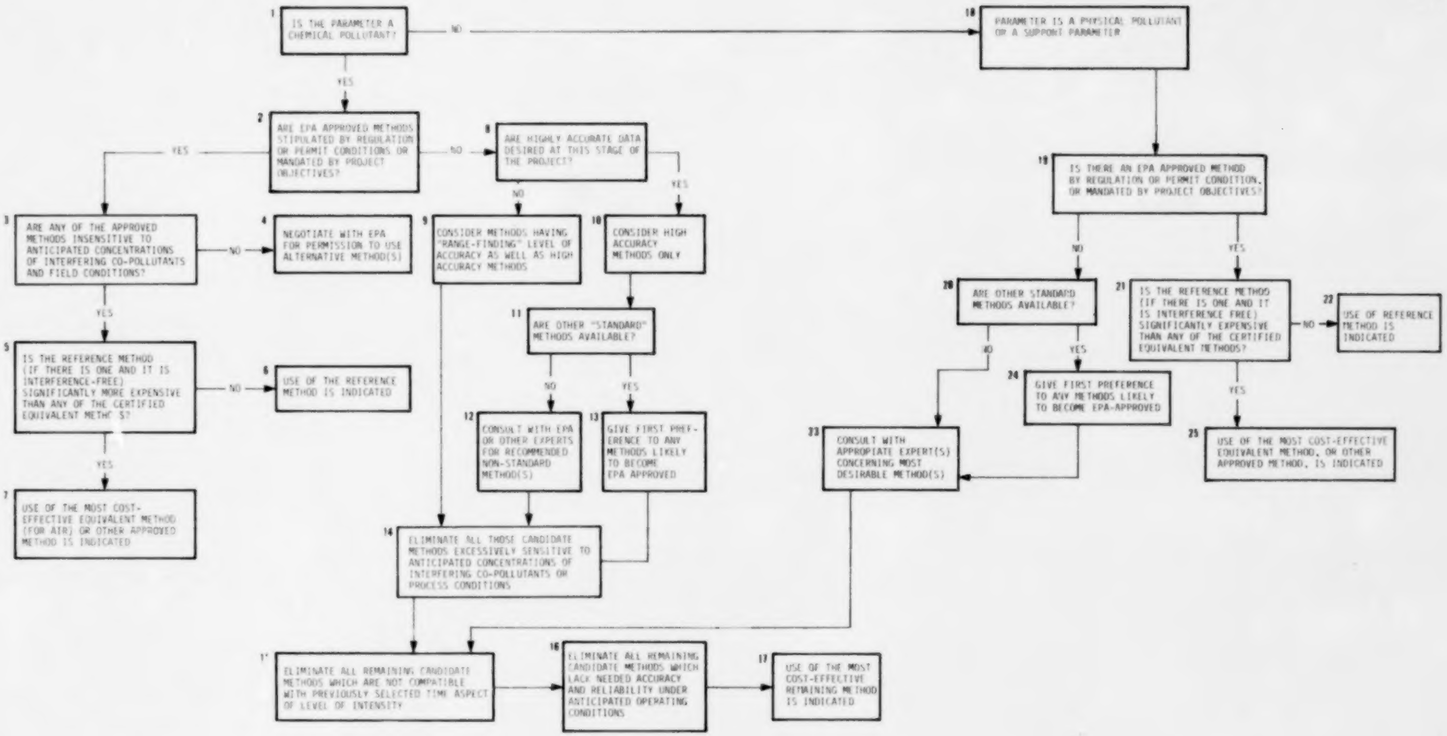
1
IS THE PARAMETER A CHEMICAL POLLUTANT?
NO
YES
2
ARE EPA APPROVED METHODS STIPULATED BY REGULATION OR PERMIT CONDITIONS OR MANDATED BY PROJECT OBJECTIVES?
YES
NO
3
ARE ANY OF THE APPROVED METHODS INSENSITIVE TO ANTICIPATED CONCENTRATIONS OF INTERFERING CO-POLLUTANTS AND FIELD CONDITIONS?
NO
4
NEGOTIATE WITH EPA FOR PERMISSION TO USE ALTERNATIVE METHOD(S)
YES
5
IS THE REFERENCE METHOD (IF THERE IS ONE AND IT IS INTERFERENCE-FREE) SIGNIFICANTLY MORE EXPENSIVE THAN ANY OF THE CERTIFIED EQUIVALENT METHC S?
NO
6
USE OF THE REFERENCE METHOD IS INDICATED
YES
7
USE OF THE MOST COST-EFFECTIVE EQUIVALENT METHOD (FOR AIR) OR OTHER APPROVED METHOD IS INDICATED
8
ARE HIGHLY ACCURATE DATA DESIRED AT THIS STAGE OF THE PROJECT?
NO
YES
9
CONSIDER METHODS HAVING "RANGE-FINDING" LEVEL OF ACCURACY AS WELL AS HIGH ACCURACY METHODS
10
CONSIDER HIGH ACCURACY METHODS ONLY
11
ARE OTHER "STANDARD" METHODS AVAILABLE?
NO
YES
12
CONSULT WITH EPA OR OTHER EXPERTS FOR RECOMMENDED NON-STANDARD METHOD(S)
13
GIVE FIRST PREF-ERENCE TO ANY METHODS LIKELY TO BECOME EPA APPROVED
14
ELIMINATE ALL THOSE CANDIDATE METHODS EXCESSIVELY SENSITIVE TO ANTICIPATED CONCENTRATIONS OF INTERFERING CO-POLLUTANTS OR PROCESS CONDITIONS
1'
ELIMINATE ALL REMAINING CANDIDATE METHODS WHICH ARE NOT COMPATIBLE WITH PREVIOUSLY SELECTED TIME ASPECT OF LEVEL OF INTENSITY
16
ELIMINATE ALL REMAINING CANDIDATE METHODS WHICH LACK NEEDED ACCURACY AND RELIABILITY UNDER ANTICIPATED OPERATING CONDITIONS
17
USE OF THE MOST COST-EFFECTIVE REMAINING METHOD IS INDICATED
18
PARAMETER IS A PHYSICAL POLLUTANT OR A SUPPORT PARAMETER
19
IS THERE AN EPA APPROVED METHOD BY REGULATION OR PERMIT CONDITION, OR MANDATED BY PROJECT OBJECTIVES?
NO
YES
20
ARE OTHER STANDARD METHODS AVAILABLE?
NO
YES
21
IS THE REFERENCE METHOD (IF THERE IS ONE AND IT IS INTERFERENCE FREE) SIGNIFICANTLY EXPENSIVE THAN ANY OF THE CERTIFIED EQUIVALENT METHODS?
NO
22
USE OF REFERENCE METHOD IS INDICATED
YES
23
CONSULT WITH APPROPIATE EXPERT(S) CONCERNING MOST DESIRABLE METHOD(S)
24
GIVE FIRST PREFERENCE TO ANY METHODS LIKELY TO BECOME EPA-APPROVED
25
USE OF THE MOST COST-EFFECTIVE EQUIVALENT METHOD, OR OTHER APPROVED METHOD, IS INDICATED

Figure 23. Methods selection-technical aspects.

permit or regulatory requirement is involved, the appropriate enforcement office personnel must be informed. If the approved methods are inaccurate due to interfering co-pollutants or field conditions, the EPA should be contacted for permission to use an alternative method (Step 4).

If the EPA-approved method is appropriate, its relative cost should be compared to certified equivalent methods (Step 5). If the approved method is not significantly more expensive, it should be used (Step 6). Otherwise, use of the most cost-effective approved or certified alternative is indicated (Step 7).

In the event that EPA-approved methods are not indicated, the desired accuracy of data for the particular stage of the project in question must be ascertained (Step 8). Standard methods as tested and approved by various professional organizations (ASTM, NBS, USGS) should be used if high accuracy is desired (Steps 10 and 11), with preference given to any standard methods which EPA may approve in the near future (Step 13). If no standard methods are available, EPA Laboratories, ASTM committees, universities, equipment manufacturers, or other research institutions should be consulted (Step 12). For various trace materials, particularly organics, sophisticated research methods and accurate equipment are available. Appropriate consultation will reveal not only possible methods for the program but also the availability of the equipment and trained personnel.

Various "range-finding" methods may be adequate when highly accurate data are not necessary, even if these methods are not sensitive or reliable enough to gain the approval of EPA or other groups (Step 9). Anticipated concentrations of co-pollutants which might interfere must also be considered for any non-EPA approved methods (Step 14).

With reference to physical and support parameters, appropriate EPA-approved methods should also be used (Steps 19, 21, 22, and 25). Where no standard or EPA-approved methods exist, certified equivalent methods should be identified through consultation with NBS, ASTM, or other sources (Step 23).

In the final steps of the methods selection, after acceptable candidate methods have been identified for each type of parameter, any method which is not compatible with the previously chosen sampling interval should be eliminated (Step 15). Methods lacking needed accuracy or reliability under actual operating conditions can also be eliminated (Step 16). Use of the most cost-effective remaining methods is indicated (Step 17).

Cost Considerations

An adequate monitoring plan carefully considers selection of parameters, methods, and sampling intensity in meeting program goals. Cost enters the decision-making process through selection of methods and sampling intensity. Unnecessarily intense sampling or use of overly sophisticated analytical methods may generate excessive total program costs.

Cost aspects of methods selection, displayed in Figure 24, involve deciding whether to use in-house or contracted services. If contracted services are considered (Steps 25-27), care should be taken to specify required method, acceptable alternatives, and level of accuracy (Step 25). The sampling route and schedule should be analyzed to identify for contract proposers the possible economies of scale resulting from multiple-sample lots of multiple-parameter methods (Step 26). Preliminary cost estimates can then be solicited from qualified contractors (Step 27).

For estimates of in-house monitoring costs (Steps 2-37), two general categories of methods are distinguished: instrumental and non-instrumental (Step 2). Instrumental methods include electronic sampling and analyzing equipment and other automated analytical methods; non-instrumental methods refer generally to "wet chemical" techniques.

For instrumental monitoring methods, the cost of purchasing or leasing various makes of satisfactory instruments is obtained first (Steps 3-4). For the use of each instrument, estimates are made of:

- Purchase or lease costs of the instrument
- Purchase or lease costs for all necessary ancillary equipment of requisite accuracy and reliability (e.g., calibrators, data loggers, and computer linkages) (Steps 5-8)
- Costs of expendable supplies for the operation of each set of primary and ancillary instruments (including computer time) (Steps 9-10)
- Costs of each type of appropriate housing needed to protect instruments from the elements, vandalism, or theft; to control temperature, humidity, and light conditions if required; or to provide mobility (Steps 11-12)
- Costs for all utility needs for each instrument set, including service lines, on-site generators, bottled

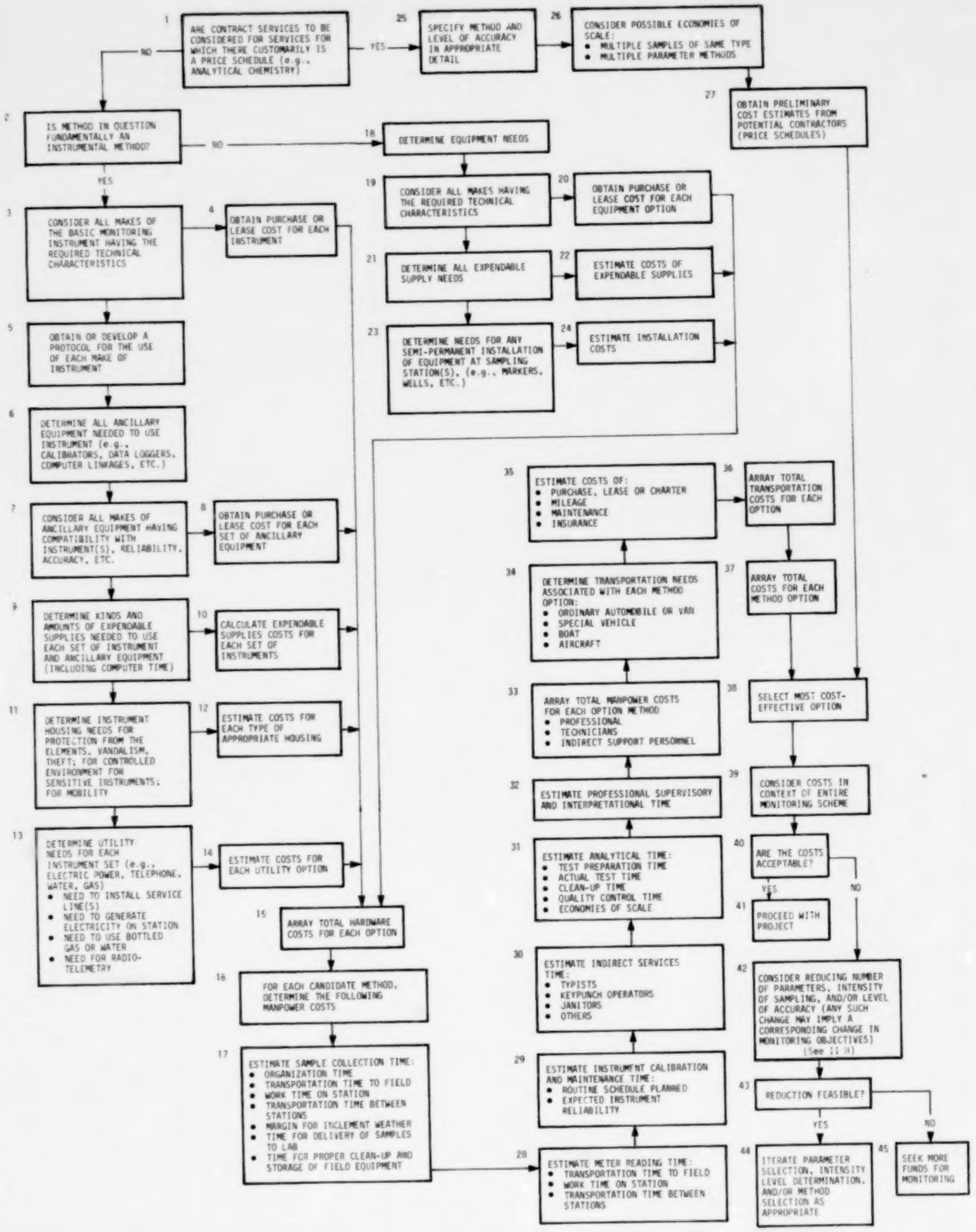
1 ARE CONTRACT SERVICES TO BE CONSIDERED FOR SERVICES FOR WHICH THERE CUSTOMARILY IS A PRICE SCHEDULE (e.g., ANALYTICAL CHEMISTRY)
YES
NO
25 SPECIFY METHOD AND LEVEL OF ACCURACY IN APPROPRIATE DETAIL
26 CONSIDER POSSIBLE ECONOMIES OF SCALE: • MULTIPLE SAMPLES OF SAME TYPE • MULTIPLE PARAMETER METHODS
27 OBTAIN PRELIMINARY COST ESTIMATES FROM POTENTIAL CONTRACTORS (PRICE SCHEDULES)
2 IS METHOD IN QUESTION FUNDAMENTALLY AN INSTRUMENTAL METHOD?
NO
YES
18 DETERMINE EQUIPMENT NEEDS
19 CONSIDER ALL MAKES HAVING THE REQUIRED TECHNICAL CHARACTERISTICS
20 OBTAIN PURCHASE OR LEASE COST FOR EACH EQUIPMENT OPTION
21 DETERMINE ALL EXPENDABLE SUPPLY NEEDS
22 ESTIMATE COSTS OF EXPENDABLE SUPPLIES
23 DETERMINE NEEDS FOR ANY SEMI-PERMANENT INSTALLATION OF EQUIPMENT AT SAMPLING STATION(S), (e.g., MARKERS, WELLS, ETC.)
24 ESTIMATE INSTALLATION COSTS
3 CONSIDER ALL MAKES OF THE BASIC MONITORING INSTRUMENT HAVING THE REQUIRED TECHNICAL CHARACTERISTICS
4 OBTAIN PURCHASE OR LEASE COST FOR EACH INSTRUMENT
5 OBTAIN OR DEVELOP A PROTOCOL FOR THE USE OF EACH MAKE OF INSTRUMENT
6 DETERMINE ALL ANCILLARY EQUIPMENT NEEDED TO USE INSTRUMENT (e.g., CALIBRATORS, DATA LOGGERS, COMPUTER LINKAGES, ETC.)
7 CONSIDER ALL MAKES OF ANCILLARY EQUIPMENT HAVING COMPATIBILITY WITH INSTRUMENT(S), RELIABILITY, ACCURACY, ETC.
8 OBTAIN PURCHASE OR LEASE COST FOR EACH SET OF ANCILLARY EQUIPMENT
9 DETERMINE KINDS AND AMOUNTS OF EXPENDABLE SUPPLIES NEEDED TO USE EACH SET OF INSTRUMENT AND ANCILLARY EQUIPMENT (INCLUDING COMPUTER TIME)
10 CALCULATE EXPENDABLE SUPPLIES COSTS FOR EACH SET OF INSTRUMENTS
11 DETERMINE INSTRUMENT HOUSING NEEDS FOR PROTECTION FROM THE ELEMENTS, VANDALISM, THEFT; FOR CONTROLLED ENVIRONMENT FOR SENSITIVE INSTRUMENTS; FOR MOBILITY
12 ESTIMATE COSTS FOR EACH TYPE OF APPROPRIATE HOUSING
13 DETERMINE UTILITY NEEDS FOR EACH INSTRUMENT SET (e.g., ELECTRIC POWER, TELEPHONE, WATER, GAS) • NEED TO INSTALL SERVICE LINE(S) • NEED TO GENERATE ELECTRICITY ON STATION • NEED TO USE BOTTLED GAS OR WATER • NEED FOR RADIO-TELEMETRY
14 ESTIMATE COSTS FOR EACH UTILITY OPTION
15 ARRAY TOTAL HARDWARE COSTS FOR EACH OPTION
16 FOR EACH CANDIDATE METHOD, DETERMINE THE FOLLOWING MANPOWER COSTS
17 ESTIMATE SAMPLE COLLECTION TIME: • ORGANIZATION TIME • TRANSPORTATION TIME TO FIELD • WORK TIME ON STATION • TRANSPORTATION TIME BETWEEN STATIONS • MARGIN FOR INCLEMENT WEATHER • TIME FOR DELIVERY OF SAMPLES TO LAB • TIME FOR PROPER CLEAN-UP AND STORAGE OF FIELD EQUIPMENT
28 ESTIMATE METER READING TIME: • TRANSPORTATION TIME TO FIELD • WORK TIME ON STATION • TRANSPORTATION TIME BETWEEN STATIONS
29 ESTIMATE INSTRUMENT CALIBRATION AND MAINTENANCE TIME: • ROUTINE SCHEDULE PLANNED • EXPECTED INSTRUMENT RELIABILITY
30 ESTIMATE INDIRECT SERVICES TIME: • TYPISTS • KEYPUNCH OPERATORS • JANITORS • OTHERS
31 ESTIMATE ANALYTICAL TIME: • TEST PREPARATION TIME • ACTUAL TEST TIME • CLEAN-UP TIME • QUALITY CONTROL TIME • ECONOMIES OF SCALE
32 ESTIMATE PROFESSIONAL SUPERVISORY AND INTERPRETATIONAL TIME
33 ARRAY TOTAL MANPOWER COSTS FOR EACH OPTION METHOD • PROFESSIONAL • TECHNICIANS • INDIRECT SUPPORT PERSONNEL
34 DETERMINE TRANSPORTATION NEEDS ASSOCIATED WITH EACH METHOD OPTION: • ORDINARY AUTOMOBILE OR VAN • SPECIAL VEHICLE • BOAT • AIRCRAFT
35 ESTIMATE COSTS OF: • PURCHASE, LEASE OR CHARTER • MILEAGE • MAINTENANCE • INSURANCE
36 ARRAY TOTAL TRANSPORTATION COSTS FOR EACH OPTION
37 ARRAY TOTAL COSTS FOR EACH METHOD OPTION
38 SELECT MOST COST-EFFECTIVE OPTION
39 CONSIDER COSTS IN CONTEXT OF ENTIRE MONITORING SCHEME
40 ARE THE COSTS ACCEPTABLE?
YES
NO
41 PROCEED WITH PROJECT
42 CONSIDER REDUCING NUMBER OF PARAMETERS, INTENSITY OF SAMPLING, AND/OR LEVEL OF ACCURACY (ANY SUCH CHANGE MAY IMPLY A CORRESPONDING CHANGE IN MONITORING OBJECTIVES) (See II H)
43 REDUCTION FEASIBLE?
YES
NO
44 ITERATE PARAMETER SELECTION, INTENSITY LEVEL DETERMINATION, AND/OR METHOD SELECTION AS APPROPRIATE
45 SEEK MORE FUNDS FOR MONITORING

Figure 24. Methods selection-cost aspects.

gas or water, and radio-telemetry (Steps 13-14). (Service roads may also be necessary.)

For non-instrumental monitoring methods, after equipment needs are determined (Step 18), estimates can be made of:

- Purchase or lease costs for each type and make of equipment (Steps 19-20)
- Costs of expendable supplies (Steps 21-22)
- Costs of obtaining and installing any semi-permanent facilities at sampling stations (e.g., markers, wells, service roads, and automatic samplers) (Steps 23-24)

These hardware costs for both instrumental and non-instrumental methods can then be arrayed and compared (Step 15).

The effort required to obtain cost estimates for all potentially applicable instruments (Step 4), equipment options (Step 20), or contractors (Step 27) is often very time-consuming and/or impractical--there may be a dozen or more suppliers of the more common types of equipment and services. However, as many cost estimates as reasonably possible should be acquired to ascertain an accurate range of costs.

If the equipment is to be purchased by competitive bidding, all identified potential suppliers will bid on supplying the necessary instrumentation and services at the lowest cost. When writing specifications for purchases through competitive bidding, it is important to note that, while the project is to obtain material which meets specifications at the lowest possible cost, some suppliers may minimize the price of their bids by proposing equipment that only marginally meets the minimum requirements in the specifications. Therefore, a vital part of writing specifications for equipment involves various technical considerations regarding the choice of the method of monitoring and the internal cost estimates, and such factors as:

- The availability of spare parts on short notice
- The availability of maintenance and repair contracts from the equipment supplier and the types of support services available
- The amount of protection available through the warranties
- Whether the equipment has been successfully used in similar projects

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- The ability of the equipment to interface with equipment on hand and on order

- Exceptions to the specifications

- The maintenance schedule and the apparent ease of equipment calibration, operation, and maintenance

- The delivery date

Bidders for major pieces of equipment and types of services should list references to independent organizations which have used their equipment and services. These users should be contacted and their viewpoints considered in the final selection.

For both instrumental and non-instrumental methods, manpower, transportation, and related costs may contain a substantial portion of the costs of the monitoring plan. There- fore, a careful examination of these costs must be made when developing the plan.

Manpower costs (Steps 16-33) require consideration of the following types of expenses as appropriate for each candidate method:

- Sample collection time--organizational efforts, portal-to-portal trip, clean-up, and contingencies (Step 17)

- Meter reading time--portal-to-portal trip (Step 28)

- Calibration and maintenance--routine and unexpected (including downtime during service by manufacturer's representative) (Step 29)

- Indirect services time--clerical, maintenance, training, and support (Step 30)

- Analytical time--preparation, analysis, clean-up, quality control; consider schedule of analysis for economies of scale (Step 30)

- Professional supervisory and interpretational time (Step 32)

These manpower costs for each alternative method can then be arrayed and compared (Step 33).

Transportation costs (Steps 34-36) for publicly owned and private vehicles include:

- Purchase, lease, charter
- Mileage and depreciation
- Maintenance
- Insurance

These, too, can be arrayed by alternative and compared.

Hardware, manpower, and transportation costs can then be combined and compared for each alternative (Step 37).

If monitoring service is contracted, all of the factors discussed above will be the concern of the contractor. The methods and level of accuracy needed are stipulated, and cost comparisons are made among various contractors' estimates (Steps 25-27).

Finally, all costs must be considered in the context of the entire monitoring scheme (Step 38). Savings in cost are sometimes possible if ambient environmental monitoring personnel and instrumentation requirements overlap with OSHA and any process monitoring resources. For example, the process work may require an analytical chemist for two-thirds of his time and the monitoring work may require a chemist on site one-third of the time; or, OSHA monitoring could require instrumentation and personnel which could be useful when measuring fugitive emissions. Where possible, these savings should be factored into cost estimates.

If anticipated costs for monitoring are too high (Steps 42- 45), reductions of the following should be considered:

- Number of pollutants and parameters
- Intensity of sampling
- Level of accuracy

Monitoring of lower-priority pollutants should be reduced or eliminated first. The proposed reductions are then considered in terms of the original program objectives. If the objectives can be met with reductions, the design and cost estimates should be revised, and the design considered complete. If the objectives cannot be met, sufficient funds to eliminate the need for reductions should be sought. If funds can be obtained, the program, as designed, is complete. If not, monitoring objectives must be redefined, and design and cost estimates revised.

CONCLUSIONS

This section focuses on the procedure for selecting pollutants generated by a facility using a FBC process for monitoring. Two approaches are possible to meet this goal for a particular problem pollutant:

- Stack/pipe monitoring with appropriate dispersion modeling
- Source-oriented ambient monitoring

The preliminary screening processes described in the first part of this section allow identification of all legal requirements for monitoring and problem pollutants. The technical and cost factors are useful in determining the appropriate mix of these alternative approaches to monitoring pollutants. Additional factors which have not been discussed but are nevertheless relevant include:

- Adequacy of sampling procedures
- Sensitivity and suitability of analytical methods
- Assumptions and models for relating source to ambient concentration levels
- Applicability and limitations of stack monitoring and modeling ambient pollutant concentrations

Finally, while ambient concentrations of some problem pollutants may be minute, exposure levels of these substances can remain potentially hazardous because of their bioaccumulation potential, potential for synergistic effects, or proximity to sensitive receivers. These substances present a serious problem in the ambient environment because the best available monitoring equipment may be incapable or detecting expected concentrations or the ambient levels of harmless chemical analogs may interfere with detection of the problem pollutant. Undoubtedly, this problem will not be resolved until FBC processes reaches commercialscale operation and effects develop that are more readily measureable.

If these factors cannot be incorporated into the priority ranking and selection procedure in an explicit and systematic fashion, their presence should, at least, influence qualitatively the monitoring system design process.

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SECTION 4

AIR QUALITY MONITORING STRATEGIES

INTRODUCTION

FBC is a coal combustion process that, in respect to air quality, emits lower quantities of gaseous pollutants for the same amount of coal burned than does a conventional pulverized coal combustion process. However, FBC can potentially emit concentrations and quantities of particulate matter higher than a conventional coal-burning plant. Most of the ash present in the coal feed to FBC is normally elutriated from the bed and must be removed (along with attrited limestone and other particulates) prior to release of the flue gas to the atmosphere.

Except for the design of the combustor, FBC is basically a variant of a conventional coal-fired plant, and therefore should be subject to the same air quality standards as any coal-fired plant. Air quality monitoring requirements and methods applicable to conventional coal-burning plants are equally applicable to FBC plants. Based on available theoretical and experimental information on air emissions from FBC plants, commercial-size FBC units will probably meet New Source Performance Standards for air emissions applicable to coal-fired facilities.

The FBC air quality monitoring strategies proposed in this section address primarily regulated pollutants, because experimental data from FBC pilot plants show that these pollutants will require monitoring. Based on available information, no other pollutants are projected to cause serious air quality problems or violate current air quality standards.

This section discusses the following important air quality parameters:

- Air quality impact generators
- Conditions where ambient monitoring may be required
- Applicable regulations and monitoring requirements
- Selection of pollutants to be monitored

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- Air monitoring network design and dispersion models
- Monitoring strategies for FBC installations

AIR QUALITY IMPACT GENERATORS

This discussion of atmospheric emissions from FBC of coal will only cover flue gas emissions, as experimental data from other sources of emissions are not available. Figure 5 in Section 2 depicts the generic FBC process scheme, and Table 4 shows the sources of atmospheric emissions. Not all of these sources will be present in all commercial units. For example, sorbent regeneration (and associated waste streams) will not be present in the first commercial FBC units currently under consideration. Furthermore, there could be some process variations involving currently undefined effluent streams. The plans for individual FBC units should be analyzed case-by-case, to develop process specific air pollutant inventories for all waste streams.

The nature and extent of fugitive atmospheric emissions from FBC processes are undefined; whether there will be significant adverse environmental impact generators of this type cannot be predicted. Table 32 explores the sources of atmospheric emissions for the FBC process. By expanding and modifying the listing in this table for each commercial-scale facility, a full air emission inventory can be developed. Some sources listed may require careful and attentive maintenance, not specialized monitoring and pollution control systems; others, occupational exposure problems contained at the FBC facility, will fall under the jurisdiction of the Occupational Health and Safety Administration rather than under the EPA.

CONDITIONS WHERE AMBIENT MONITORING IS INDICATED

The variations in processes which could be used and types of pollutants which may be generated as a result of FBC technology are summarized in Section 2. The complex operations at a facility employing FBC as an energy conversion process will determine the need for and requirements of a source-oriented monitoring program. Two basic types of atmospheric emissions can be identified: stack emissions and fugitive emissions.

Each process associated with FBC technology should be monitored for fugitive and stack emissions, and, as well, for wastes generated by processes not directly generated by an FBC facility. In some cases, pollutant discharges may be altered by contaminants introduced by the FBC process, e.g., in cooling towers or cooling ponds gaseous or aerosol discharges could contain enhanced or altered pollutant levels due to contamination by wastes associated with the FBC process.

TABLE 32. SOURCES OF ATMOSPHERIC EMISSIONS

Activity	Source
Coal Preparation and Feed	Shipping Coal to Plant Coal Unloading Fugitive Emissions During Storage Loading of Coal to Preparation Plant Crushing, Sizing, Washing, Drying, Fine Particulate Removal or Preparation to Recycle Materials Handling in Coal Preparation Plant Coal Feed Hopper Backflow
Coal Combustion and Associated Pollution Control	Normal Stack (Flue) Gas Stack (Flue) During Soot Conditions Blowing Stack During Start-Up Stack Gas Particulate Removal--Hopper Unloading Stack (Flue) Gas Particulate Storage Stack (Flue) Gas Particulate Recycling Coal Feed Materials Handling
Stack (Flue Gas) Particulate Disposal	Stack Gas Particulate Loading for Transport Stack Gas Particulate Transport Stack Gas Particulate Unloading and Processing at Disposal Site Stack Gas Particulate Storage at Disposal Site Stack Gas Particulate Use in Commercial Application
Special Start-Up	Start-Up Combustion of Coal, Liquid Fuel, or Gas Air Preheater (if any) with liquid or gaseous fuel
Leaks	Fugitive Emissions from Leaks in Boiler and Directly Associated Systems
Sorbent Preparation and Feed	Sorbent Shipping Sorbent Unloading Sorbent Storage Sorbent Loading to Preparation Plant Sorbent Preparation - crushing - sizing - washing - drying - fine particulate removal or preparation for recycle Material Transfer in Sorbent Preparation Plant Sorbent Feed Hopper Backflow
Spent Sorbent Discard	Bed Solids Removal from Active Boiler Used Bed Solids Storage Waste Bed Solids Transfer for Shipping Waste Bed Solids Shipping Waste Bed Solids Unloading and Processing at Disposal Site (or Use Site) Waste Bed Solids Storage at Disposal Site Waste Bed Solids Use in Commercial Application

(Continued)

TABLE 32 (Continued)

Activity	Source
Sorbent Regeneration Unit Operations	Unloading Bed Solids to Regenerator
	Bed Solids Regeneration Flue Gas
	Regeneration Flue Gas Fine Particulate Collector Hopper Unloading
	Regeneration Flue Gas Shipment
	Regeneration Flue Gas Fine Particulate Disposal (or Use)
	Regeneration and Sulfur Recovery
	- bed solids regeneration sulfur recovery system stacks (stacks and vents)
	- sulfur unloading
	- Sulfur storage
	- Sulfur shipment
	- Sulfur unloading at disposal site
	- sulfur disposal or use
	- sulfur recovery fugitive emissions
	Fuel for Regeneration
	- fuel shipment
	- fuel storage
	- fuel preparation
	- fuel combustion
	- ash collection
	- flue gas particulate collection
	- flue gas particulate disposal
	- ash disposal
	- special gases used for regeneration
Maintenance	Bed Shutdown Solid Waste Removal
	Solids Bed Cleaning
	Removal of Solids from Metal Cleaning and Scraping
	Plant Maintenance Fugitive Emissions
	- cleaning
	- lubrication
	- repair
Steam Turbine and Water Treatment Unit Operations	Cooling Tower Plume (or Cooling Pond)
	Gas from Turbine
	- stack
	- fugitive
	Turbine Gas Pollution Control System Solids Disposal
	Boiler Blowdown Water Off-Gases
	Cooling System Cleaning Gases and Suspended Particulates
	Steam System Cleaning Gases and Particulate Matter
	Other Processes Using Steam from Boiler
	Blowdown from Water Treatment Operations
	Gas Turbine Fugitive Emissions

Disposal of the solid wastes generated by the FBC technology would require at the very least a source monitoring program during disposal operations and at the site after covering the solids with soil or other material. Monitoring programs at the disposal site should be directed towards measuring amounts of fugitive emissions resulting from handling of the solid wastes at the landfill site, and monitoring for potential gases or fumes generated by bacterial or chemical action upon the FBC solid wastes or combination wastes.

In the absence of evidence that they will not constitute a significant problem, effluent streams should be monitored. The need for testing should be determined case-by-case and the reasons for not testing (and for testing) documented, based on the inventory of effluent streams. An effluent stream may not require monitoring if:

- Data from similar or related facilities indicate that the process stream is not a problem. (The applicability and limitations of applying data from other sources to the specific installation must be considered before such a decision can be adequately justified.)
- Emission factors for pollutants are not available. The limitations of the data base and the need for site-specific information should be considered in this determination.
- Control systems included in the specific installation will render the impact of the effluent insignificant. In this case, the need for verification of the effectiveness of the control system, the impact of control system failure, and of byproducts of control should be considered.

In some cases, while it may be desirable to monitor an effluent stream, there may be mitigating reasons why monitoring is not carried out:

- It may be considered too expensive or not cost-effective.
- The parameters to be studied are unmeasurable by current technology, or the accuracy of such measurement is unknown.

REGULATIONS

New Source Performance Standards

Federal New Source Performance Standards (NSPS), published by the EPA, for atmospheric emissions from all fossil-fuel-fired plants are summarized in Table 33, which is derived from 40 CFR Part 60.

Some states have regulations and individual emission standards for boilers smaller than 73 megawatts that are tighter than the above restrictions. Often, these regulations are generated on a case-by-case basis to assure compliance with state-wide ambient air quality standards, Prevention of Significant Deterioration (PSD) regulations, or emission offset regulations. During the following conditions, the NSP Standards do not apply: during startup; during shutdown; or during emergency conditions when sulfur dioxide emissions are minimized by operating all flue gas desulfurization modules that can be operated (with a spare module for units larger than 365 megawatts (1,250 million Btu/hr) under some circumstances).

Owners and operators of federally regulated FBC steam generators must install, calibrate and maintain an SO_2 emission monitoring system and record its output. For electric utility FBC units, an "as fired" fuel monitoring system is also required for measuring potential SO_2 emissions before control (SO_2 monitoring upstream of control equipment is not applicable to FBC units for which SO_2 is controlled in the combustion chamber).

The owners and operators also must install, calibrate and operate a continuous monitoring system for CO_2 or O_2 at locations where SO_2 is monitored. This allows the readings of the SO_2 emission monitor to be converted to ng/J. For units equipped with CO_2 monitoring, the formula is:

$$E = C_d F_c \left(\frac{100}{\%CO_{2d}}\right) \text{ or } E = C_w F_c \left(\frac{100}{\%CO_{2w}}\right) \qquad (20)$$

where:

E = Pollutant emission rate, ng/J

C = Pollutant concentration, ng/scm on a dry or wet basis (Subscripts "d" or "w" are used to note this)

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TABLE 33. FEDERAL STANDARDS OF PERFORMANCE FOR NEW STATIONARY SOURCES OF AIR POLLUTION

Source category	Affected facility	Pollutant	Emission level	Monitoring requirement
Subpart D:				
Fossil fuel fired steam generators >73 MW heat input (>250 million Btu/hr), 63 Kcal/hr)	Coal-fired boilers	Particulate	0.10 lb/million Btu	No requirement
		Opacity	20% (27% for 6 min/hr)	Continuous
		SO_2	1.20 lb/million Btu	Continuous
		NO_x		Continuous
		Anthracite, Bituminous, or Subbituminous coal	0.70 lb/million Btu	
		Lignite	0.60 lb/million Btu	
		More than 25% coal refuse	Exempt	
Subpart Da:				
Electric utility steam generating units >73 MW heat input (>250 million Btu/hr)	Coal-fired boilers (and coal-derived fuels)	Particulate	0.03 lb/million Btu	No requirement
		Opacity	20% (27% for 6 min/hr)	Continuous
		SO_2	1.20 lb/million Btu and 90% reduction, except 70% reduction when emissions are less than 0.60 lb/million Btu	Continuous compliance
		100% anthracite	Percent reduction does not apply	
		NO_x		Continuous compliance
		Anthracite, Bituminous, and Lignite	0.60 lb/million Btu	
		Subbituminous coal	0.50 lb/million Btu	
		Coal-derived fuels and shale oil	0.50 lb/million Btu	
		More than 25% coal refuse	Exempt	
Subpart Y:				
Coal preparation plants	Thermal dryer	Particulate	0.031 gr/dscf (0.070 g/dscm)	Temperature scrubber pressure loss Water pressure
		Opacity	20%	No requirement
	Pneumatic coal cleaning equipment	Particulate	0.018 gr/dscf (0.040 g/dscm)	No requirement
		Opacity	10%	No requirement
	Processing and conveying equipment, storage systems, transfer and loading systems	Opacity	20%	No requirement
Subpart HH:				
Lime manufacturing plants	Rotary lime kilns	Particulate	0.30 lb/ton	Scrubber pressure loss; Scrubber liquid supply pressure
		Opacity	10%	Continuous

$\%CO_2$= Percent carbon dioxide on a dry or wet basis, depending on the subscript

F_c = A factor representing the ratio of the volume of carbon dioxide generated to the calorific value of the fuel combusted. F is defined as follows:

- for anthracite, $F_c = 0.532\times10^{-7}$ scm CO_2/J
- for subbutuminous and bituminous coal, $F_c = 0.486\times10^{-7}$ scm CO_2/J
- for lignite $F_c = 0.516 \times 10^{-7}$ scm CO_2/J
- special formulas are given for mixtures of different fuels

In chemically active FBC units, some CO_2 is emitted and some O_2 is removed when limestone is converted to calcium oxide in the boiler, causing a slight systematic underestimation of the ng/J emissions when the above formulas are used. These effects are of minor significance under normal operating conditions, but should be considered, along with the errors in monitoring, in borderline cases between compliance and non-compliance with emission regulations.

All federally regulated FBC installations are required to process the stack monitoring data and report any emissions above those allowable by the standards. For electric utility steam generators, the reporting of running 30-day average ng/J emissions and percent reduction in potential emissions is also required.

Prevention of Significant Deterioration

The Clean Air Act Amendments of 1977 contain comprehensive requirements for the prevention of "significant deterioration" of air quality in areas that have pollution levels better than the national ambient air quality standards. Such areas may be classified as Class I, Class II or Class III, according to the amount of deterioration of air quality allowed. Table 34 shows the maximum allowable increases. For any period, other than an annual period, the applicable maximum may be exceeded no more than once per year at any location. Allowable increases in annual average levels may never be exceeded.

It is possible to obtain a presidential or gubernatorial variance in Class I areas, providing that certain allowable increments for SO_2 are not exceeded more than 18 times per

TABLE 34. ALLOWABLE INCREASES IN AMBIENT POLLUTION LEVELS UNDER PSD REGULATIONS

Pollutant	Area designations[a]		
	Class I (μg/m^3)	Class II (μg/m^3)	Class III (μg/m^3)
Particulate Matter			
Annual Geometric Mean	5	19	37
24-Hour Maximum	10	37	75
Sulfur Dioxide			
Annual Arithmetic Mean	2	20	40
24-Hour Maximum	5	91	182
3-Hour Maximum	25	512	700
Carbon Monoxide[b]			
Nitrogen Oxides[b]			
Ozone[b]			
Visibility[c]			

[a] Class I is defined by EPA as environmentally "pristine"; Class II as approaching EPA pollution maximums; Class III as "all others."

[b] Federal regulations currently under development.

[c] Visibility regulations were proposed by EPA in the Federal Register (45 FR 34762) on May 22, 1980. Final versions have not been promulgated but are expected to differ from the proposed versions. This phase of the regulations addresses Federal Class I regions only. Future phases are expected to address regional haze and plume controls.

year. The allowable increase in low terrain areas is a 24-hour value of 36μg/m^3 and a 3-hour value of 130 μg/m^3. In high terrain, it is a 24-hour maximum of 62 μg/m^3 and a three-hour level of 221 μg/m^3. In addition, the air pollution levels may never exceed any applicable ambient air quality standard (see Table 35).

TABLE 35. AMBIENT AIR QUALITY STANDARDS[a]

Pollutant	Duration	Restriction	Federal Standards Primary	Federal Standards Secondary
Suspended Particulates	Annual Mean[b]	Not to be exceeded	75	60
Suspended Particulates	24 hour mean Concentration	Not to be exceeded more than once per year	260	150
Sulfur Dioxide	Annual Mean	Not to be exceeded	80 (.03)	-
Sulfur Dioxide	24 hour mean Concentration	Not to be exceeded more than once per year	365(.14)	-
Sulfur Dioxide	3 hour mean Concentration	Not to be exceeded more than once per year	-	1300(.50)
Lead	3 month Mean	Not to be exceeded	1.5	1.5
Carbon Monoxide	8 hour mean Concentration	Not to be exceeded more than once per year	10(9.0)[c]	10(9.0)[c]
Carbon Monoxide	1 hour mean Concentration	Not to be exceeded more than once per year	40(35.)[c]	40(35.)[c]
Photochemical Oxidants	1 hour mean Concentration	Not to be exceeded more than once per year	235(.12)	235(.12)
Non-methane Hydrocarbons	3 hour mean Concentration	Not to be exceeded between 6:00 AM and 9:00 AM	160(.24)	160(.24)
Nitrogen Dioxide	Annual Mean	Not to be exceeded	100(.05)	100(.05)

[a] Unless otherwise noted, values without parentheses are in micrograms per cubic meter. Values in parentheses are in parts per million by volume.

[b] Geometric mean. All other averages are arithmetic means.

[c] Values without parentheses are in milligrams per cubic meter.

All areas with air quality better than the ambient air quality standards are classified as Class II (except for certain kinds of national and international parks) unless state governments (or the Indian governing body, in the case of an Indian reservation) follow specified procedures to have the area reclassified, to allow for development. The SO_2 increments are applicable to the combined impact of all new sources in an area operating after the date of the first application for a permit subject to PSD regulations. Compliance with the increments is generally determined by modeling, and compliance with the ambient air quality standards is determined by superimposing the modeled impact of the sources on observed background ambient air quality concentrations.

All new major emitting facilities must obtain a PSD permit before they are built. Such facilities include new, isolated FBC facilities with a heat capacity above 250,000,000 Btu/hr (when used as steam electric power plants or boilers) which have the potential to emit more than 100 tons/year of any regulated air pollutant when control equipment is operating in a reasonably anticipated manner. In other applications, the limit is 250 tons/year. All sources at an installation, including fugitive sources, may be included in the total tonnage, at the discretion of the EPA Regional Administrator. No current EPA regulations explicitly cover atmospheric fugitive emissions from coal combustion solid waste disposal operations.

If an FBC unit is built at an existing facility, and an existing source at the facility is shut down or otherwise modified so that there is no net increase in emissions, a PSD permit would not be required. Retrofitting an existing boiler with FBC technology may also result in an exemption if there is no net increase in emissions. Appropriate emission factors for fugitive atmospheric emissions from FBC solid waste handling activities are not available. Fugitive emission testing before and after modification would be appropriate to provide a data base for such determinations in cases where significant increases in emissions are possible. Requiring full PSD monitoring, unless the source can demonstrate no significant impact, might also be considered on a case-by-case basis.

Monitoring Requirements

When necessary, new sources subject to the PSD regulations are required to monitor the ambient air quality for up to 1 year to establish that the impact will not cause or contribute to an exceedance of the ambient standards. Monitoring for less than 1 year may be acceptable if it demonstrates to the satisfaction of the regulatory agencies involved that the standards will not be exceeded. If adequate data are already available to establish background levels, monitoring may not be required.

If there are no significant man-made sources nearby, certain background levels may be assumed constant (see Table 36). Although background particulate levels can be far above 40 $\mu g/m^3$ during dust storms, these background levels can be used to allow construction of new facilities, without emission offsets or other sometimes impractical controls, in areas where standards are exceeded because of dust storms.

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(PREVIOUSLY CIN. EPA FORM 287)
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TABLE 36. ASSUMED NATURAL BACKGROUND CONCENTRATIONS (EPA, 1978b)

Pollutant	Concentration (μg/m^3)
SO$_2$	20
CO	1
NO$_2$	.01
Total Suspended Particulates (TSP)	30-40
O$_3$	--

The EPA also has the authority to require ambient air quality monitoring after a source is built to establish the effects of the source on ambient pollution levels. Seldom used, this authority might be appropriate in areas where the theoretical impact of a source combined with the background is only marginally better than the standards, and the uncertainty in modeling or fluctuations in annual average levels from other sources might mean that there actually are exceedances. It might also be appropriate if the impact of a source can be separated from background levels and if there is considerable uncertainty in the appropriateness of the model or the emission factors used for determining PSD increment consumption. EPA has the authority to require a rollback of operations or application of retrofit air pollution control technology if it is determined that PSD increments are being exceeded.

Maximum ground level concentrations from isolated point sources in simple, relatively flat terrain can typically be predicted to within a factor of two or three, using the equations in the EPA Workbook of Atmospheric Dispersion Estimates (Turner, 1974) or the UNAMAP computer program package (Briggs, G., to Cornett, C.L., personal communication). The exact location of the maximum may differ from the modeling; accuracy only to an order of magnitude is not unusual when predictions are made for a specific location. If there are no conditions that the modeling did not account for (e.g., lake-effect-induced fumigations, particle settling, reactions and washout of gases, or plume behavior in complex terrain), higher accuracy may be possible.

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The amount of error in the ability to separate the impact of a source of interest from background concentrations needs to be considered if increment consumption caused by a source is to be monitored. Fluctuations in background air pollution levels can occur that cannot be accounted for by simply comparing total pollution concentrations before and after a plant is built. Some form of tracer for the plant may be needed when the background is significant. Fluctuations in background air pollution levels are dependent on variations in emission rates from background sources and on meteorological conditions. Monitoring over several years' time is usually required to measure these long-term fluctuations.

Legal requirements for PSD monitoring are contained in 40 CFR Parts 51, 52, 53 and 58 (Federal Register, August 7, 1980), and additional general guidance is available from the PSD Guidelines (EPA, 1978a). The Guidelines cover all aspects of PSD monitoring, including network design, instrument selection and operation, quality assurance and data reporting. Generally, monitoring is performed to represent levels where the source has its maximum impact and where the source plus the maximum background is maximum. For SO_2 monitoring, the 3-hour and 24-hour maximum impact is recommended. When fugitive emissions could be significant, monitoring at the site of the proposed facility is also recommended. The exact number and location of stations must be determined on a case-by-case basis by the owner or operator and reviewed by the permit-granting authority. A major limitation of the PSD Guidelines is that they do not cover monitoring network design in any detail. Available references should be consulted (Ball and Anderson, 1977; Ludwig et al., 1977; Ludwig and Shelar, 1978).

SELECTION OF POLLUTANTS TO BE MONITORED

Introduction

The procedures described in Section 3 were followed, where applicable, to select pollutants for air quality monitoring of the commercial-scale FBC process. The review of impact generators and regulations described in this section formed the basis for determining how the pollutant selection procedure had to be modified for air quality monitoring.

It is assumed that future commercial-scale FBC processes will be subject to the same air quality standards as those which apply to conventional coal-fired plants. Furthermore, commercial units will probably meet the New Source Performance Standards for air emissions.

Categorization and Prioritization

Currently, data are unavailable for estimating expected ambient concentrations of air pollutants generated by FBC units similar to commercial-size conventional coal-fired boilers. Therefore, no Category III pollutants were identified for priority ranking. The preliminary list of pollutants contains only Category I and Category II pollutants and parameters. Once data become available to complete a full air emission inventory of a commercial-scale facility and disposal sites, Category III pollutants can be identified and added to the preliminary list to determine the need for additional monitoring.

Category I Pollutants--

The Category I chemical pollutants and parameters, and the reference documentation are listed below (specific values for each standard and detailed descriptions of present monitoring requirements were previously noted.)

Pollutant or air quality parameter	Source
Opacity of flue gas particulate emission rate reduction in SO_2 emissions CO_2 or O_2	NSPS for fossil-fuel-fired steam generators 40 CFR 60.4 to 60.44
Opacity of all emissions particulate emissions	Federal standards for new coal preparation plants 40 CFR 60.250 to 60.254
Particulate matter SO_2	Clean Air Act Amendments (1977); Prevention of Significant Deterioration of Air Quality
Suspended particulates SO_2 Pb CO Ozone Non-methane hydrocarbons NO_x	Ambient Air Quality Standards

Most of these pollutants, with the exception of the ambient air quality standards (Table 35), will require, primarily, emission monitoring of the FBC source. The implications of these standards to development of a source-oriented ambient air quality monitoring program for an FBC unit is discussed in the section, "Monitoring Requirements."

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Category II Pollutants--

Category II pollutants identified for the FBC process (carbon monoxide, nitrogen oxides, ozone, and visibility) are given in Table 34 with expected promulgation dates.

Estimation of Expected Ambient Concentration of Problem Pollutants--

Since the primary problem air pollutants are already regulated, priority ranking based on expected ambient concentrations is not required, nor possible, because of the lack of emission data. However, dispersion modeling procedures appropriate for estimating maximum ground level concentrations from isolated FBC sources are discussed below.

Preliminary List of Pollutants for Monitoring

The air pollutants and air quality parameters identified through the selection protocol are listed in Tables 34 and 35. Only Category I and Category II pollutants can be identified, based on currently available information.

AIR MONITORING NETWORK DESIGN AND DISPERSION MODELS

Background

Most evaluations of the impact of point sources on ambient air quality employ process data, emission factors, and meteorological data to predict ambient concentrations through dispersion modeling. Sometimes, determining which meteorological data and dispersion model to employ can be quite controversial, and a wrong choice can lead to errors.

This can be illustrated with reference to the June 12, 1979, Federal Register in which EPA proposed relaxing the SO_2 emission regulations for two power plants located along the southern shore of Lake Erie (EPA, 1979b), because source-oriented ambient monitoring allegedly showed that the urban RAM model (used to derive the emission regulations for the plants) was inappropriate. The plant owners indicated that the rural RAM model seemed more appropriate, and their environmental consultant did not believe lake-effect-induced fumigation was important in contributing to exceedances of the ambient air quality standards.

EPA is proposing to require the installation of an extensive ambient air pollution monitoring network to help verify that the reviewed emission limitations will protect the ambient air quality standards or to develop an appropriate data base for establishing new emission limitations, if the revised limitation does not. The details of this monitoring program have not been announced by the EPA, but the plant owners plan to install ten stationary air pollution monitoring stations for each power plant affected.

Ambient air pollution monitoring can easily be misused, underestimating the true peak impact of an individual installation. Detailed EPA guidelines and regulations--stating what constitutes an acceptable program for checking the accuracy of air pollution models and how to petition for changes in emission regulations--are needed. In the absence of such guidelines and regulations, the following discussion presents some general guidance.

Air Monitoring Network Design

Whenever possible, meteorological data spanning at least a 5-year period should be used to design the monitoring network. The monitoring stations, ideally, should be placed at locations where the maximum impact of the source is predicted, according to the different models being studied. Peak 3-hour and 24-hour impacts are usually the most important for point sources. Since the locations where these impacts occur change from year to year, these differences should be considered in monitoring network design and data interpretation. This will allow some flexibility in locating monitoring stations.

A series of stations should be placed along radial lines emanating from the source, at distances where the various models being tested predict measurably different ambient pollution concentrations. This will help to facilitate selecting the most accurate model. Available information and guidance should be considered for all pollutants of interest emitted directly from the source (Ball and Anderson, 1977) and for further refinement and expansion of the monitoring station network (evaluating, upgrading, enforcing, and assessing supplementary control systems) (EPA, 1976a; 1976b). The monitoring methods and probe placement should conform to the requirements for state and local air monitoring stations.

The ability to separate the impact of the source or sources of interest from background levels must be given adequate consideration in monitoring program design. Sometimes, the use of tracers may be necessary; if so, the toxicity of these materials should be considered.

At a minimum, meteorological towers and equipment, adhering strictly to requirements and recommendations (Nuclear Regulatory Commission, 1972) should be employed, with one exception. Bivanes (or approved equivalent) meeting all NRC specifications in the horizontal plane, extended to the vertical plane, should be used. The data should be processed to generate the usual wind direction and the velocity data used in modeling and direct estimates of the σ_y and σ_z values. Horizontal and vertical wind direction should be read by a data processor at least once every ten seconds and processed to determine the appropriate standard deviations over the three-minute to one-hour time periods most models are meant to represent (the exact time will depend on the model). After computing σ_y and σ_z (Pasquill, 1974), the values of σ_y and σ_z can be compared to the values predicted from the models and the meteorological data sources used to model impacts to determine if they are appropriate. They can also be used directly in modeling.

Caution should be exercised in interpreting the applicability of the resulting monitoring data, especially near large bodies of water and in complex terrain, where the representativeness of meteorological data can be quite limited. There can be large localized shears in wind direction and changes in turbulence that are relatively unpredictable, without an adequate observational data base to study the detailed climatology. Under such circumstances, it can be appropriate to use certain types of advanced instrumentation such as:

- Acoustic radar to measure mixing heights.
- Doppler acoustic radar to measure winds aloft. Tristatic rather than bistatic systems are recommended (when possible) in complex flow regimes to assure that the vector wind parameters are for the same parcel of air.
- Laser doppler anemometers.
- Tethered balloons (wiresondes) with wind direction, velocity, air temperature, and wet bulb temperature, with telemetry. These can be operated on automatic winches to provide vertical profiles. They can also be operated at plume centerline height. These devices are also useful for temporary installations aimed at studying complex wind fields over an area.
- Pilot balloons (pibals) tracked by balloon theodolites (with lights for use at night, when needed).
- Rawinsondes tracked by radar or radio direction finders.
- Radiosondes to transmit vertical wet bulb, dry bulb, and pressure soundings to ground stations.
- Rocketsondes.

- Aircraft with monitoring equipment for air temperature, relative humidity, turbulence (to pinpoint thermal inversion boundary layers for fumigation studies), pollution, infrared ground and water temperature, and recording navigational equipment.

- Mobile air pollution monitoring vehicles, with pollution monitoring instruments, calibrators, SO_2 remote sensing devices (correlation spectrometers), wet and dry bulb temperature recording, navigational equipment, event recorders, data loggers and computers for practical real-time displays of the monitoring results (EMI MAP system), all of which work while the vehicle is in motion.

- Semi-mobile air monitoring vans that can be dispatched to a site to immediately begin measuring pollution levels for up to 24 hours when parked. It should have power onboard to keep instruments warmed up in transit and either a network of power drops or other power supply for use when parked. If generators are used for power when parked, care must be taken that the system does not measure its own exhaust.

- Stationary SO_2 remote sensors for measuring plume rise.

The aircraft sampling and ground-based SO_2 sending can be used to measure σ_y and σ_z values and plume rise (although problems may arise when multiple intersecting plumes are involved unless they are mixed completely). They can also be used to dispatch the mobile ground based pollution monitoring vehicles to locations of maximum plume impact.

The exact set of equipment and monitoring program must be determined on a case-by-case basis. In one case, a network of ten stationary SO_2 monitoring stations, selected on the basis of a study of lake effect, was deployed around a power plant in Waukegan, Illinois, on the shore of Lake Michigan (Dooley, 1976; Lyons, 1977). A single mobile van under aircraft guidance measured 11 SO_2 samples above 0.15 ppm on the field, while the 10 stationary sites together measured only 1. This suggests that, if the purpose of ambient monitoring around a source is to measure compliance or non-compliance with standards, the possible existence of unobserved peak concentrations should be considered in the data interpretation, along with the amount of error in the data. The extensive meteorological and mobile monitoring conducted also revealed significant details about the lakeshore meteorology and atmospheric dispersion that could not be obtained by more conventional stationary air pollution monitoring techniques.

In addition to ambient pollution monitoring and meteorological sensing, a model validation study using a real pollution source should include continuous monitoring of the types of process data to be used to project future emissions, and the continuous monitoring of effluent emission rates, volume rates of flow, and effluent temperature. The latter two can be used to calculate plume rise, to allow comparison with observed plume rise. Measurement of moisture and major gas constituents in the stack can also be valuable in plume rise calculations. The specific heat and phase changes in effluents can have significant effects. Remote sensing equipment can be quite useful for the direct measurement of plume rise; sampling with aircraft can also be appropriate.

The cost of extensive monitoring programs should be balanced against the value of the data generated, to determine if it is worth the expense. It is difficult to ascribe a dollar value to the protection of human life or to an aesthetically pleasing environment. Professional judgment must be exercised in such situations, to assure the most cost-effective program to obtain the needed information.

For guidance on past monitoring verification models, consult Mills and Stern (1975) and Mills and Record (1975).

MONITORING STRATEGIES FOR FBC INSTALLATIONS

Background

The air quality monitoring programs for commercial-scale installations for FBC of coal fall into five categories: 1) baseline monitoring prior to construction, 2) Level 1 and Level 2 assessment monitoring, 3) compliance audit monitoring, 4) source monitoring required by current regulations of all coal-fired facilities/boilers and 5) fugitive emission monitoring. The first category is well regulated and currently implemented at federal, state, and local levels and need not be addressed in this report. The second category is a research approach that has use in initial operational environmental assessment of new commercial FBC installations. The other three require different strategies implementable through source-oriented ambient monitoring filling informational and system gaps created by some inherent shortcomings of emission monitoring systems.

Compliance Audit Monitoring

Compliance audit monitoring is performed periodically to assure that source monitoring systems are producing valid data and that the source is complying with applicable emission standards.

A serious deficiency in the emission monitoring requirements is that they do not include comprehensive quality assurance auditing programs to quantify the precision and accuracy of the data. For extractive gas monitoring systems, reactive gases are more sensitive to systematic losses due to contamination of in-stack filters and other forms of contamination of extractive systems than CO_2. In addition, extractive systems can leak (especially when in-stack filters are clogged). This can cause systematic underestimation of lbs/10^6 Btu emission rates. Even without the systematic errors, random errors can occur in the data.

At an absolute minimum, all quality assurance and quality control procedures required and recommended for Prevention of Significant Deterioration (PSD) monitoring should be performed. In addition, auditing the accuracy of the gas monitoring systems by introducing calibration gas at the sample line inlet should be mandatory because of the possibility of systematic losses of reactive pollutant gases or leaks between the environment and the detectors. The temperature of the lines should be kept above the dew point, using heated sample lines, if necessary. The appropriate state and local agency should also perform compliance audits.

Following are some stack monitoring problems, in addition to leaks and contamination of sampling systems (Floyd, 1979):

- Design specifications of instruments in stacks often are not closely checked by agencies or users of stack monitoring equipment.
- Agencies do not always check instrument and probe placement on a stack.
- Performance specifications are not always met when the equipment is operating.
- Several years may pass between the initial performance evaluation for a stack monitoring system and the next evaluation.

A quality assurance audit of the system design and installation should be performed, supplemented by a spot check of system performance. Some value can be derived from compliance audit stack tests using federal reference methods and auditing by challenging the instrument, as close to the probe tip as possible, with known concentrations of the gases being monitored. It would also be useful to supplement the "in-stack" auditing programs with non-intrusive compliance auditing techniques. The techniques for doing this may not be as accurate as in-stack methods, but they might provide reasonable grounds to obtain warrants for definitive stack tests in the event of a gross problem with the in-stack measurements. The compliance audit values would have to be compared to the reported in-stack data or to the hourly data that sources are required to record. Comparing the reported data with that which could be reasonably anticipated from the type of equipment in use is recommended.

Several techniques for performing such auditing are presented below. Further research is necessary, however, to validate these techniques.

Methods of Measurement--

Ratio of Components Techniques--There is no mechanical separation between the molecules of CO_2 and SO_2 , which are both part of the emission from coal-fired power plants. There can be chemical transformations, adsorption and absorption of the gases at different rates, but these are often slow. Typical rates of CO_2 loss are much slower than for SO_2. If the concentration of SO_2 and CO_2 caused by a source can be separated from background concentrations close enough to the stack to minimize transformations, the ratio of these concentrations in the ambient environment might be used to measure emission rates. The technique also applies to particulate and oxides of nitrogen, when compared to carbon dioxide.

Upwind/Downwind Sampling--

Upwind/downwind sampling works best when the concentration caused by the source is far above background levels, to damp out the importance of fluctuations in background concentrations. Samplers could be hoisted into smoke plumes, and upwind of smoke plumes, to measure these concentrations. Aircraft, kites, tethered balloons or cranes could be used to hoist the necessary monitoring equipment into plumes. Naturally, there can be problems if several sources share the same stack.

Differential Plume Impact Monitoring--

The differential plume impact technique involves ground level monitoring of SO_2 and CO_2. Monitoring stations are located around the source, according to the site location criteria for source-oriented ambient monitoring (Ball and Anderson, 1977), to minimize the background effect on the readings when the wind is coming from the direction of the source being monitored. SO_2 and CO_2 levels are monitored and recorded continuously by fast-response instruments. Ideally, the response times and characteristics from background levels to plume centerline concentrations should be the same for both instruments (or adjusted numerically to be the same during data processing). By measuring the amount of change in SO_2 and CO_2 concentrations as the source plume sweeps back and forth across the monitoring site, the relative concentrations of SO_2 and CO_2 caused by the source can be measured. Areas under peaks might also be used.

The results of a similar measurement program in Frankfurt-am-Main, Germany, are illustrated in Figure 25 (Weber, 1970). Meteorological and pattern recognition techniques are used to identify the concentration peaks caused by the source. While there is considerable variation in the CO_2 to SO_2 ratios, enough statistics might be gathered after a 30-day period to average out the variations. Since SO_2 is generally removed from the air faster than CO_2, emission rates are underestimated.

In Germany, the measured ambient ratios were compared to the ratios measured in the stack to help measure removal rates for SO_2 from power plant plumes. The data were sorted according to wind direction, velocity, stability, class and relative humidity as part of the program. Very rapid removal rates (over 50 percent per hour of transit time) were measured in the highly polluted Frankfurt-am-Main area (Weber, 1970). Typical loss rates for relatively clean environments with low relative humidities are less than five percent per hour in other studies using other techniques (Koch et al., 1977). Similar studies could be performed around conventional power plants in the United States with reliable in-stack monitoring programs.

The differential plume impact technique could, in principle, be adopted to study NO_x emission rates. Continuous monitoring of total NO_x and CO_2 levels would be needed for this purpose. Monitoring of NO and CO_2 levels in the ambient environment and in stacks could yield information on NO to NO_2 conversion rates (especially if supplemented with continuous NO_2 or NO_x measurements). Potential advantages of the technique are its low cost and that artificial tracers need not be injected into plumes to study transformations. Limitations include:

- A variable systematic error may result in emissions being underestimated if transformations are not accounted for.
  (If transformations were modeled and emissions "back calculated", large random errors could be introduced.)

- Applying the technique to an individual boiler at a plant with several boilers may be difficult. (There can also be problems if it is used to study emissions from the plant as a whole.)

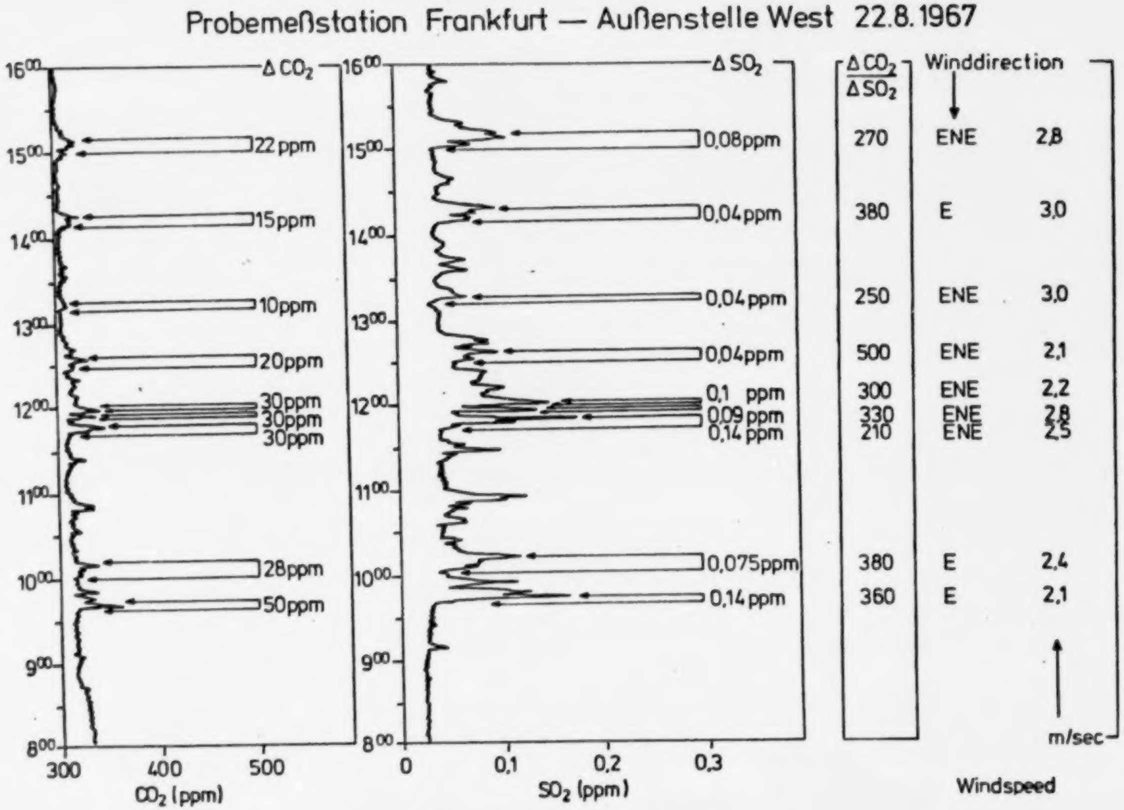

Figure 25. Differential plume impact data.
(Weber, 1970)

- If stationary ambient air monitoring is used, the surveillance is not continuous. Any significant short-duration variations in emission rates from FBC units make it difficult to compare the results to average hourly reported or recorded emission rates. The magnitude of these variations needs to be studied, to help provide some information on the limitations of grab samples and of such spot tests. Monitoring from a vehicle using ratio of components technique of data processing as the vehicle passes through the plume could provide many measurements during an hour, but significantly increase the expense of the technique.

- The peaks caused by a power plant may not be easily separated from other peaks caused by background sources, especially in the winter for some installations.

- When performing plume transformation studies, transformation rates may differ in various parts of the plume, e.g., studies indicate that the removal rate for SO_2 in power plant plumes is higher at the edges of the plume than at the center (Koch et al., 1977).

Remote Sensing--Various optical devices are commercially available, or under development, for the remote measurement of SO_2 at the mouth of smoke stacks and/or in the ambient environment. Most such devices are passive, measuring only the amount of SO_2 in "line of sight." This is known as the SO_2 "burden," and is measured in micrograms per square meter. As of Summer 1979, SO_2 laser radar units were experimental, expensive, not available as standard commercial units, and require more field testing. In addition, some dual absorbance systems may not have the full-scale range necessary to measure concentrations at the mouth of smoke stacks.

Equipment for the remote measurement of CO_2 is rarely available, even experimentally. Instruments such as the Barringer Non-Dispersive Gas Filter Spectrometer can be set up for CO_2, but the utility of the device has not been demonstrated in power plant studies. Background CO_2 levels exceed 300 ppm, and it could be difficult to detect a plume against the background with a device that only measures the amount of CO_2 in line of sight. The dependence of the response of a two-channel infrared to the temperature of the gas could also cause some difficulties. As an alternative, Fourrier Transform Interferometer (FTIR) with a telescope could be aimed above the mouth of smoke stacks and next to the stack for background measurements. This device could discriminate between stack CO_2 and background CO_2 by the changes in absorption band characteristics caused by the temperature of the effluent. The changes in spectral characteristics can also be used to measure effluent temperature. Remote sensor mobile FTIR devices are expensive ($150,000 for a working mobile system) and require highly trained operating personnel. Nevertheless, testing of the accuracy and limitations of FTIR for this purpose could be worthwhile. The EPA has used its mobile FTIR to investigate sources for enforcement purposes, and demonstrating its utility and limitations for quality assurance auditing could be of some value. The device might also be used to measure SO_2 concentrations, although an error of 5°C in temperature can cause a 20-percent error in concentration.

In the absence of established methods for measuring CO_2 concentrations and burdens in power plant plumes remotely, some information can be derived from measurement techniques for SO_2. Concentrations measured at the mouth of a stack can be compared to in-stack measurements. If the in-stack monitor measures $\mu g/m^3$ at stack conditions, the measurements at the mouth of the stack could be compared directly (provided it is not diluted before exiting the stack). If it measures $\mu g/m^3$ at standard temperature and pressure, or ppm, correction to stack effluent temperature would be needed before data can be compared. If the measurements are made per dry cubic foot, correction for moisture would also be needed (or the amount of error from not considering it would have to be considered in data interpretation).

Instruments that measure the burden of SO_2 and which scan across the mouth of smoke stacks can be used to measure effluent concentrations. The measurements from such instruments can be converted to emission rates by multiplying the concentrations by the volume rate of flow out the stack. Emission rates can also be calculated from the velocity of the gas exiting the stack and the concentration of materials in the plume. Laser doppler anemometers and the Viviplume remote sensor are two instruments capable of measuring effluent velocity to calculate volume rates of flow, although the accuracy and limitations of the devices need further study.

SO_2 emission rates can also be measured by remote sensors that measure the burden of SO_2 overhead. Measurements of the overhead SO_2 burden can be combined with data on the wind direction and velocity in an area surrounding the plant, and the matter flux of SO_2 in and out of the area can be calculated. The difference is the SO_2 emission rate minus the decay rate in the area. These emission rates can then be compared to the maximum allowable emission rates and to the emission rates assumed in emission inventories.

The types of data required to make these comparisons are:

- Design assumptions for the plant concerning the boiler efficiency
- Test reports during start-up of the boiler concerning the efficiency under various percentages of capacity loads
- Records on the source of the coal, the Btu/lb rating, the percent sulfur (or at least the maximum percent sulfur, and the amount burned (if available)
- Pounds of steam produced, its temperature, flow rate and pressure.

There is no reason to believe that a remote sensor that works for conventional boilers without significant interferences will not work for FBC units. One test of this assumption is to use a remote sensing spectrometer or interferometer to measure the spectral "signature" of the plume. The spectrum could be checked for interfering gases such as absorbance bands due to other gases. If they are not present, the applicability of the remote sensor would be established for similar sources. It is necessary to obtain average spectrum because a single slow scan would have problems with turbulent eddies in the plume and fluctuations in concentration and plume geometry during scanning FTIR. Many remote sensors operate in the visible/ultraviolet region where instruments similar to FTIR are not available within EPA; however, some university astronomy departments or other organizations such as NASA may be able to provide appropriate instrumentation. If 3-minute scans with a relatively high resolution visible/ultraviolet spectrometer were integrated and averaged over a long enough period, any significant fluctuations could be dampened out.

An alternative test would be simply to repeat experiments used to establish the applicability of the remote sensor for conventional boilers to FBC units. Generally, in-stack measurements for parameters of interest, using federal reference methods or the equivalent, when possible, are compared to the results of remote measurements. The best experiments involve independent teams taking the stack measurements and the remote sensing measurements and interpreting the results, and a referee compiling and comparing the results and coordinating the timing of the tests. Duplicate simultaneous measurements of in-stack and remote measurements could be used to establish the amount of precision in the measurement methods. The cost of such a program would probably be less than that of developing visible/special ultraviolet spectral scanning data processing techniques; however, the latter techniques could be useful for many other types of sources than FBCs and are faster.

Dispersive Correlation Spectroscopy--The operating principle of dispersive correlation spectrometers is summarized as follows (Moffat and Millan, 1969):

> The principle of correlation spectrometry is based on measurement of the degree of similarity between the molecular absorption spectrum of a chosen gas and the actual absorption spectrums of the gases under observation. A correlation spectrometer system typically consists of a light source, field-defining fore-optics, an entrance slit, collimating elements, dispersive element, exit mask, and photodetector. Radiant power from the light source is focused on the entrance slit, dispersed by a prism or grating, and refocused in the plane of the exit mask. The incoming spectrum is then made to cross-correlate against the mask by moving one relative to the other in some cyclical fashion and collecting the output on a photodetector. The exit mask is an enhanced and modified replica of the absorption spectrum of the gas being sought and is usually made by depositing a film of aluminum on quartz or glass blank and then stripping or photoetching a series of slits in the aluminum which correspond in some predetermined fashion with the molecular absorption bands of the desired spectrum.

The sensitivities of some remote sensing correlation spectrometers are as follows (set with an 8-second integration time) (Lawrence-Berkeley Laboratory, 1976):

Instrument	SO_2 ppm-meter	NO_2 ppm-meter
COSPEC II	6	3
COSPEC III	6	3
COSPEC IV	2	1

The COSPEC dispersive correlation spectrometer, operated as a passive SO_2 and/or NO_2 remote sensing system, may be useful in experimental studies, for mapping plumes, dispatching mobile air sampling equipment, measuring σ_y and σ_z values in model verification studies, and measuring emission rates. The sensor, mounted in a vehicle equipped with recording navigational equipment, usually measures the burden overhead and is driven around the source to be monitored. The resulting readings, in grams per square meter of SO_2 and/or NO_2 in line of sight overhead as a function of vehicle position, are converted to pollutant mass emission rates, using meteorological data (preferably at plume centerline height and close to the position of the measurements, especially the position of the plume). Pibals and wiresondes are the most common devices for measuring wind direction and velocity, although stationary meteorological towers or laser anemometers may also be used.

There are interferences to the SO_2 burden readings from correlation spectrometers. Among the major characteristics of the instrument that need to be considered for accurate results are:

- The device may measure different wave lengths at once. As a result, the response characteristics vary with the spectral distribution of the background light. Adjustments can be made to the instrument to minimize the baseline drift caused by changes in sky spectral radiance (Millan and Hoff, 1976). The unit can also recalibrate very quickly to compensate for changes in sky spectral radiance during the day. These instruments do not work at night.

- The COSPEC II and III respond to changes in the polarity of the background light relative to the detector. This can cause problems when circling a source, especially when the sun is within 30° of the horizon. Certain internal adjustments can be made to minimize this problem: the unit can be rotated during traverses to maintain the same polarity angle to the sun, or optical devices can be inserted in the field of view to randomize the polarity at a sacrifice in the amount of signal into the instrument (Millan, M.M., Barringer Research, to Cornett, C.L., personal communication).

- The angle of view of the telescopes on the units, while adequate for most sky viewing, is finite. If an object or feature of the sky is smaller than the angle of view, it acts like its own slit and changes the response of the instrument. This can cause serious problems when viewing plumes exiting smoke stacks from too far back. Also, under these circumstances, varying distances through the plume and the background will be read simultaneously and the automatic gain control will not compensate properly for correlated non-homogeneous light intensities and SO_2 burdens in the field of view. When viewing across smoke stacks, the size of the field of view must be considered when determining how far back to place the instrument. When viewing the sky, recording of the automatic gain control can be used to edit out extraneous peaks caused by cloud fringes on partly cloudy days. Recalibration is required with changing sky conditions.

- Cloud fringe spikes are also caused because the instrument combines two channels of measurement with different time constants.

- There is very little ultraviolet background energy near the horizon--the atmosphere is heavy in the ultraviolet spectrum. Measurements should be made at least 15° above the horizontal.

- Under high particulate loadings, light may be scattered into the field of view of the instrument that has been affected by SO_2 before this scattering. This effect is usually less than 10 percent of the apparent $\mu g/m^2$ readout.

- Different instruments have different full-scale concentration ranges, depending on the mask chosen and degree of tuning. The response also becomes non-linear for high SO_2 burdens. It is necessary to choose the proper mask, instrument and tuning combination for the application. The masks are not easily changed.

- The instrument has a finite and adjustable response time that must be considered when setting up for a given application. This sometimes is important in data interpretation.

In an EPA-sponsored study at a coal-fired power plant (Sperling, 1975), a 95 percent confidence of the results being within ± 20 percent of simultaneous in-stack monitoring of SO_2 emission rates was obtained using standard EPA methods. This study involved circling the power plant 30 to 85 times over 2 to 6 hours, measuring the SO_2 burden overhead as a function of vehicle position, and tracking many balloons to gather meteorological data. The COSPEC II yielded this confidence in two hours; the COSPEC III and IV in about 6 hours. More recent work yielded the following approximate differences in emission rates relative to reference methods for a power plant emitting more than 60 metric tons per day of SO_2, using COSPEC II and III instruments (Sperling et al., 1979):

- ± 50 percent in single traverses

- ± 35 percent for 20-minute averages or 2 to 5 traverses

- ± 20 percent for 60-minute averages or 4 to 13 traverses

- ± 10 percent for 7 to 12-hour averages or 25 to 75 traverses.

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Instrumental inaccuracies, fluctuations in real source emission rates, and especially the non-representativeness of meteorological data at one location or along a trajectory (for balloon wind measurements) compared to real conditions at the locations where the remote sensor is viewing, contribute to measurement errors. Nevertheless, the applicability and accuracy of correlation spectroscopy has been reasonably established.

A COSPEC II remote sensor has been used in at least one study scanning across the mouth of a smoke stack to measure SO_2 concentrations for comparison to in-stack measurements (Table 37). At a range of 20 meters, the results look encouraging; at more distant ranges, large discrepancies are apparent. It is believed that the cause of the problem is the size of the field of view compared to the size of the stack. More work of this sort needs to be performed. The sensitivity of the correlation spectrometer should be more than adequate for even the smallest commercial-size FBC units, at the mouth of the stack. It could be necessary to desensitize the instrument so that it is not too sensitive in stack mouth applications.

Non-Dispersive Gas Filter Correlation Spectrometer (GFC)--

This device uses cells containing various amounts of the pollutant gas to be measured to modulate light signals between a telescope and light detectors. An ultraviolet SO_2 remote sensor, commercially available in France, costs less than \$10,000, versus around \$25,000 for a COSPEC IV. Its accuracy and performance have not been established.

A Science Applications Incorporated instrument works in the infrared region, with an 8-milliradian field of view. The sensitivity and noise of the device varies with the temperature of the gas being monitored. Table 38 presents some results of the use of an early prototype of the instrument to measure gas concentrations at the mouth of smoke stacks, compared to concentrations measured within the stack.

Ultraviolet Television Sensor--

An ultraviolet television-based remote sensor for SO_2 concentrations, emission rates, and effluent velocity has been developed by the National Aeronautics and Space Administration and is commercially available for less than \$33,000. The instrumentation system measures the opacity of the SO_2 exiting the stack, converts it to effluent concentration, tracks SO_2 eddies to measure the average effluent velocity, and calculates the resulting mass emission rate. The sensitivity is about 50 ppm meters. It also supplies a television image of

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TABLE 37. COMPARISON OF IN-STACK AND COSPEC II SO_2 CONCENTRATION MEASUREMENTS
(Lugwig and Griggs, 1976)

Range (meters)	In-Stack (ppm)	Remote (ppm)	$\frac{(IS) - (REM)}{(IS)} \times 100$
20	500	465	7
20	585	520	10
200	700	240	65
300	460	224	52
300	450	205	54
300	700	275	60

TABLE 38. SUMMARY OF AVERAGE VALUES OF REMOTE GFC AND EXTRACTIVE DATA
(Ludwig and Griggs, 1976)

			$[SO_2]$, ppm				
					Extractive[a]		
Range (m)	Date	Time	Remote T, C	Remote Conc.	DuPont Analyzer	EPA Method 6	% Deviation
160	8-12-74	10:00-11:45	150	540+200	---	---	
390	8-12-74	13:45-16:50	150	630±170	---	525+25	-17
390	8-13-74	09:00-12:00	150	530±120	---	398±23	-25
390	8-13-74	18:45-21:00	150	550±120	412+18	---	-25
390	8-14-74	09:15-12:45	150	490±160	422±28	401+17	-16
390	8-14-74	14:30-16:30	150	440±110	472±32	475±7	+ 7
160	8-15-74	09:30-11:45	110	750± 70	519±21	499±11	-32

[a] All extractive data taken from plume with a temperature of 150 ± 5°C.

the SO_2 plume. Plume visualization can be used to assess plume geometry and check for downwash. Such phenomenon could cause inappropriate path lengths to be used for calculating concentrations from opacities, if unobserved. To operate the unit, the inside and outside stack diameter is fed into the keyboard, the unit is calibrated, the camera is pointed at the black target, the distance to the target is fed in, and the camera is then pointed at the stack. Cursors are set around the outside stack diameter using the TV image (to scale the results). The unit can then be commanded to measure concentrations, velocities and emission rates once or repeatedly every minute to every 5 minutes and to print the results.

It would be desirable to program the microprocessor to output hourly average values also, but the lack of this feature is only a minor inconvenience. Table 39 compares the results of monitoring using a prototype unit and EPA reference methods at 400 meters. The results were extremely close to the EPA reference method results.

TABLE 39. COMPARISON OF SO_2 CONCENTRATION AND EFFLUENT VELOCITY MEASUREMENTS BY VIDEO AND IN-STACK TECHNIQUES
(Exton, 1977)

Date	Concentration, ppm			Velocity, m/sec		
	Video	UV (in-stack)	Method 6	Video	LDV	Method 2
8/3/76	790	650	740	22.8	--	22.7
8/4/76	860	660	840	21.6	19.1	22.4

In extremely polluted environments, background plumes, non-uniform background particulate light scattering, and high opacity plumes may present some problems.

Emission Rates for Other Materials--

While certain types of remote sensors can give information on emission rates of certain pollutant gases of interest, they will not work for all gases, nor for trace materials within particulates. The National Center for Atmospheric Research in Boulder, Colorado, has been applying a technique for studying emission rates from volcanoes. Sulfur dioxide emission rates were measured with a COSPEC correlation spectrometer mounted in an airplane equipped with inertial navigation equipment and meteorological instrumentation. The ratios of the concentrations of other chemicals and components to SO_2 in the volcano plume were determined by sampling the plume from the airplane. Emission rates for materials of interest were then calculated by multiplying the SO_2 emission rate by the ratios.

This basic technique should be validated by applying it to measure emissions from air pollution sources, while conventional stack monitoring is taking place, and comparing results. Once its accuracy and limitations are documented, the technique may be considered for FBC units.

Similar techniques to those described for SO_2 monitoring are also applicable to NO_x monitoring. The main limitation is that most of the NO_x emitted from sources is in the form of NO, and most remote sensors measure NO_2 rather than NO.

Level 1 and Level 2 Assessment Monitoring

The EPA Industrial Environmental Research Labs has developed a detailed approach to effluent characterization (Lentzen et al., 1978). The basic approach is to characterize effluents in three phases of increasing specificity and accuracy:

- Level 1 - Identify pollutants in specific waste streams (and fugitive emissions) with an accuracy factor of ±3; no special procedures are employed to obtain statistically representative samples or analyses.
- Level 2 - Focus on waste streams indicated as potentially troublesome; characterized by statistically representative samples, accurate stream flow measurements, and quantitative identification of specific organic species and/or classes and inorganic elements and/or species
- Level 3 - Identify critical components in selected waste streams using Level 2 or better methods as a function of time and process variation for control device development.

Figure 26 illustrates the Level 1 analysis scheme; Table 40 shows the basic Level 1 analyses. The source assessment sampling system (SASS) used to test ducted emissions is presented in Figure 27. Grab samplers are also used. Figures

TABLE 40. BASIC LEVEL 1 ANALYSES
(Lentzen et al., 1978)

Category	Parameter
Physical	Cyclone particle size
	Optical microscopy
Chemical	Spark source mass spectrometry (SSMS)
	Atomic absorption spectroscopy (AAS)
	Wet chemical (selected anions)
	Gas chromatography (GC)
	Elution chromatography (LC)
	Ion chromatography (IC)
	Infrared spectrometry (IR)
	Low resolution mass spectrometry (LRMS)
	Total chromatographable organic (TCO)
Biological	Rodent acute toxicity
	Microbial mutagenesis
	Cytotoxicity
	Fish acute toxicity
	Algal bioassay
	Soil microcosm
	Plant stress ethylene

28 and 29 outline the types of analysis performed on the material collected in the ducted effluents, and Figure 30 shows a schematic diagram of the Fugitive Air Sampling Train (FAST). FAST provides a 500 mg sample in 8 hours for unenclosed emissions that cannot be measured by the SASS train and is used in upwind/downwind sampling (Kolnsberg, 1976).

FAST separates particles into four size ranges:

- Those greater than 100 microns, separated on the louvers at the inlet. These are not ordinarily measured because they are too big to usually be blown far from the source.

- Those greater than 15 microns and less than 100 microns. These are separated on an impactor in the diaphragm. The impactor is to be replaced by a settling chamber elutriator because the performance of

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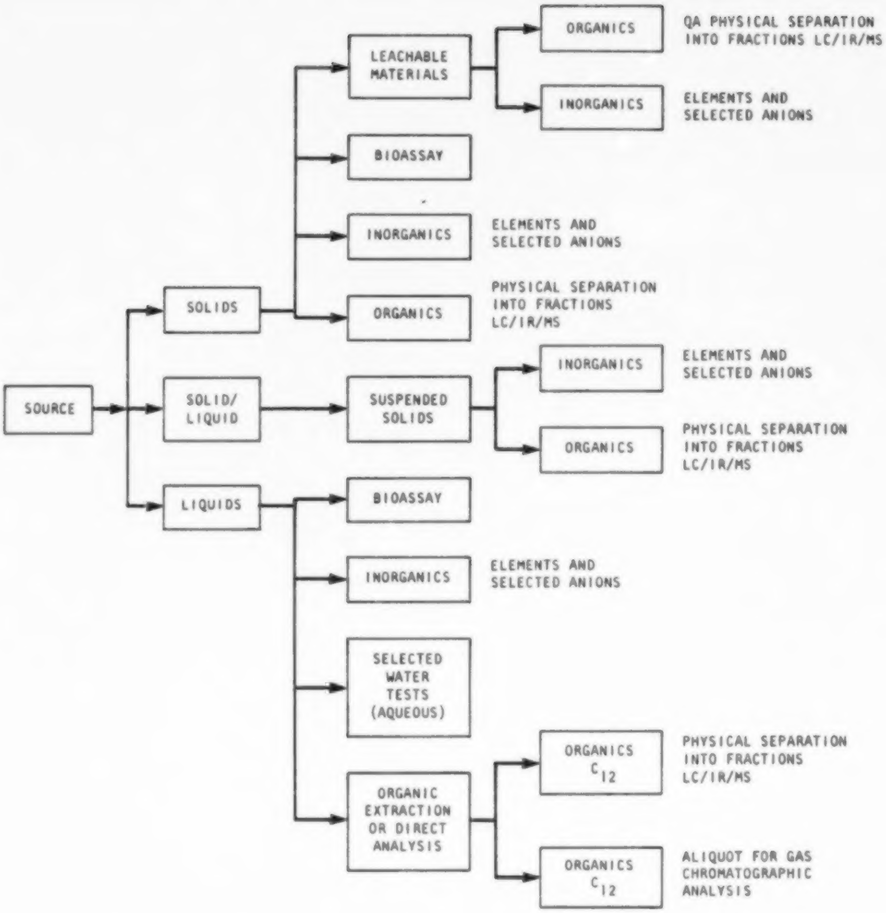
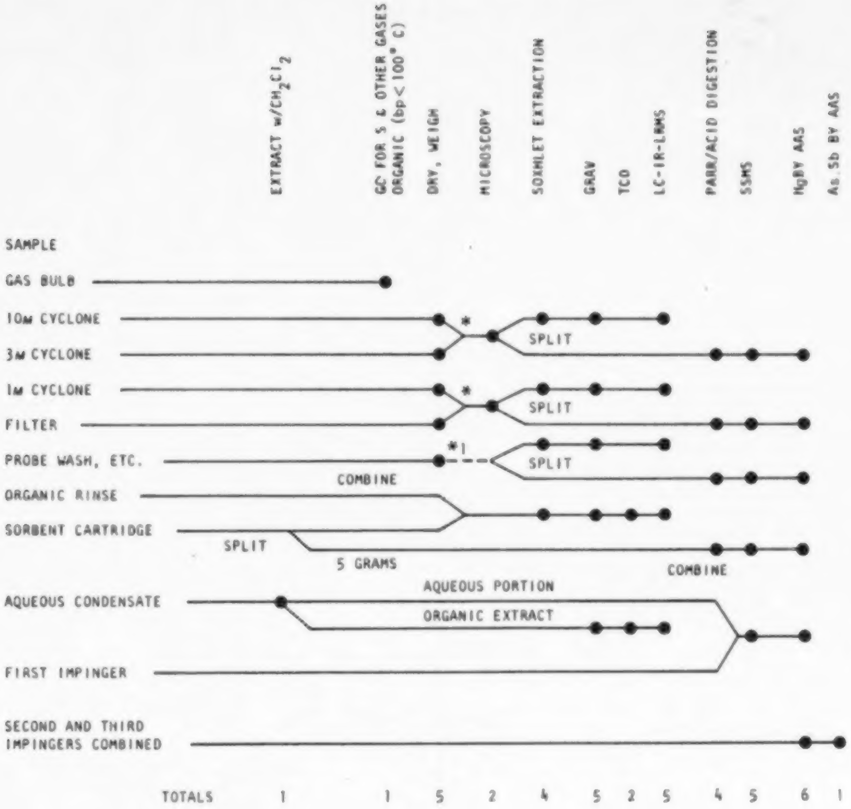

SOURCE
SOLIDS
SOLID/ LIQUID
LIQUIDS
LEACHABLE MATERIALS
ORGANICS
QA PHYSICAL SEPARATION INTO FRACTIONS LC/IR/MS
INORGANICS
ELEMENTS AND SELECTED ANIONS
BIOASSAY
INORGANICS
ELEMENTS AND SELECTED ANIONS
ORGANICS
PHYSICAL SEPARATION INTO FRACTIONS LC/IR/MS
SUSPENDED SOLIDS
INORGANICS
ELEMENTS AND SELECTED ANIONS
ORGANICS
PHYSICAL SEPARATION INTO FRACTIONS LC/IR/MS
BIOASSAY
INORGANICS
ELEMENTS AND SELECTED ANIONS
SELECTED WATER TESTS (AQUEOUS)
ORGANIC EXTRACTION OR DIRECT ANALYSIS
ORGANICS C12
PHYSICAL SEPARATION INTO FRACTIONS LC/IR/MS
ORGANICS C12
ALIQUOT FOR GAS CHROMATOGRAPHIC ANALYSIS

Figure 26. Basic level 1 sampling and analytical scheme for solids, slurries, and liquids.


EXTRACT w/CH2Cl2
GC FOR S & OTHER GASES ORGANIC (bp < 100° C)
DRY, WEIGH
MICROSCOPY
SOXHLET EXTRACTION
GRAV
TCO
LC-IR-LRMS
PARR/ACID DIGESTION
SSMS
HgBY AAS
As,Sb BY AAS
SAMPLE
GAS BULB
10µ CYCLONE
3µ CYCLONE
1µ CYCLONE
FILTER
PROBE WASH, ETC.
ORGANIC RINSE
SORBENT CARTRIDGE
AQUEOUS CONDENSATE
FIRST IMPINGER
SECOND AND THIRD IMPINGERS COMBINED
*
SPLIT
*
SPLIT
*1
SPLIT
COMBINE
SPLIT
5 GRAMS
COMBINE
AQUEOUS PORTION
ORGANIC EXTRACT
TOTALS 1 1 5 2 4 5 2 5 4 5 6 1

* If required, sample should be set aside for biological analysis at this point.

[1] This step is required to define the total mass of particulate catch. If the sample exceeds 10% of the total cyclone and filter sample weight, proceed to analysis. If the sample is less than 10% of the catch, hold in reserve.

Figure 27. SASS analysis requirements.
(Lentzen et al., 1978)

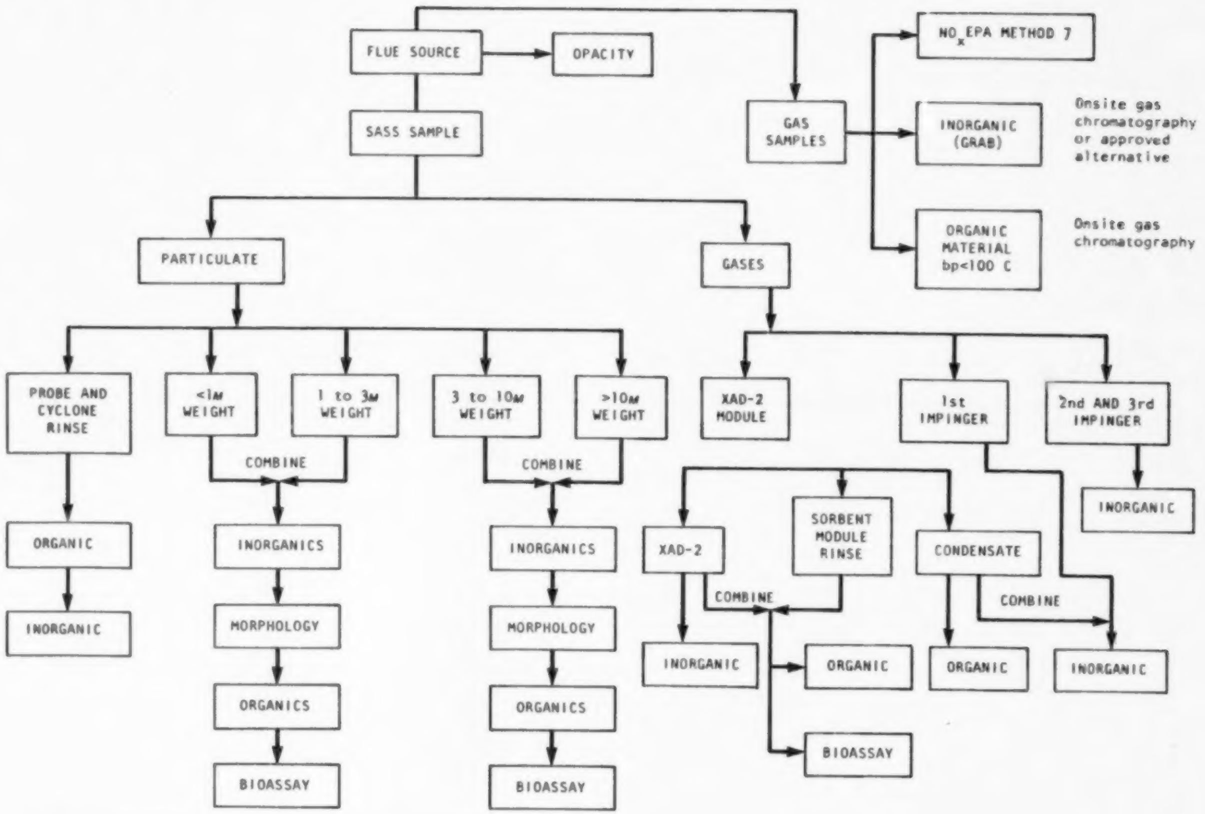

FLUE SOURCE
OPACITY
SASS SAMPLE
GAS SAMPLES
NO$_x$ EPA METHOD 7
INORGANIC (GRAB)
Onsite gas chromatography or approved alternative
ORGANIC MATERIAL bp<100 C
Onsite gas chromatography
PARTICULATE
GASES
PROBE AND CYCLONE RINSE
<1μ WEIGHT
1 to 3μ WEIGHT
3 to 10μ WEIGHT
>10μ WEIGHT
XAD-2 MODULE
1st IMPINGER
2nd AND 3rd IMPINGER
COMBINE
COMBINE
ORGANIC
INORGANIC
INORGANICS
MORPHOLOGY
ORGANICS
BIOASSAY
INORGANICS
MORPHOLOGY
ORGANICS
BIOASSAY
XAD-2
SORBENT MODULE RINSE
CONDENSATE
COMBINE
COMBINE
INORGANIC
ORGANIC
BIOASSAY
ORGANIC
INORGANIC
INORGANIC

Figure 28. Flue gas sampling flow diagram.
(Lentzen et al., 1978)

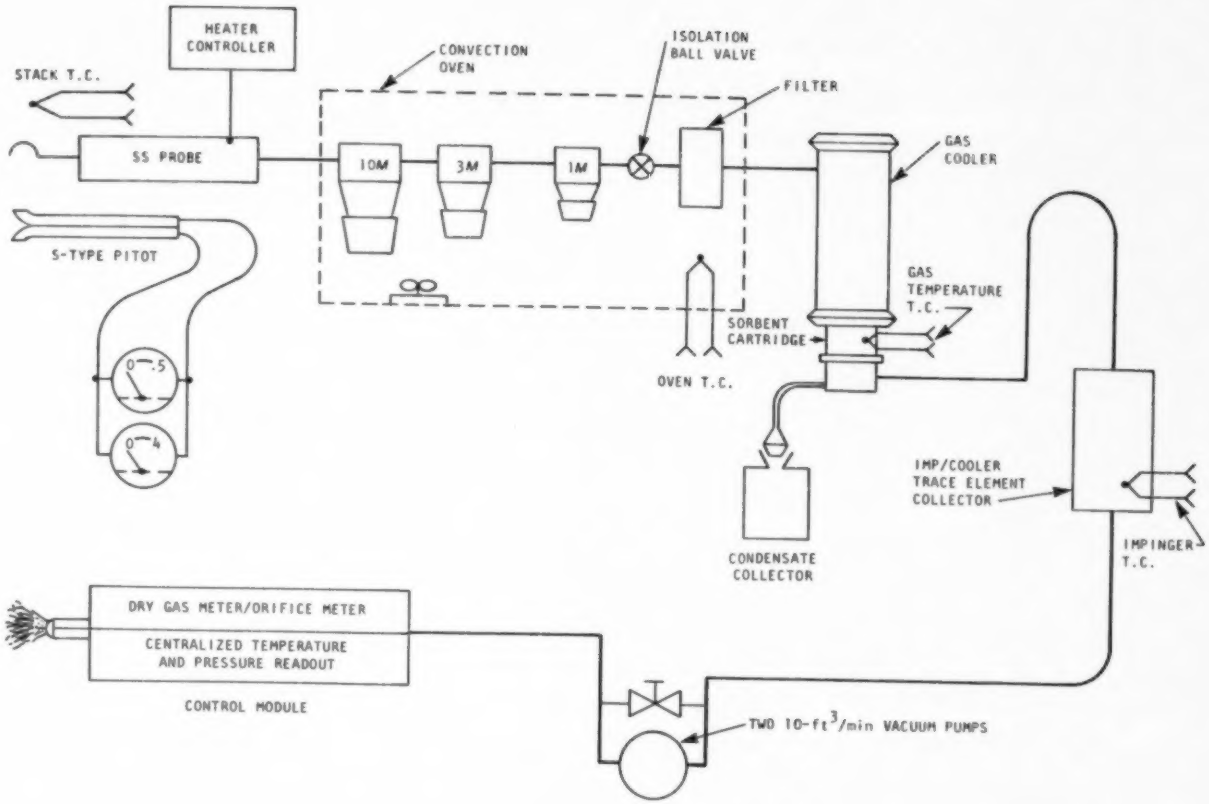

HEATER CONTROLLER
STACK T.C.
SS PROBE
CONVECTION OVEN
10M
3M
1M
ISOLATION BALL VALVE
FILTER
GAS COOLER
S-TYPE PITOT
0 .5
0 4
OVEN T.C.
GAS TEMPERATURE T.C.
SORBENT CARTRIDGE
CONDENSATE COLLECTOR
IMP/COOLER TRACE ELEMENT COLLECTOR
IMPINGER T.C.
DRY GAS METER/ORIFICE METER
CENTRALIZED TEMPERATURE AND PRESSURE READOUT
CONTROL MODULE
TWO 10-ft³/min VACUUM PUMPS

Figure 29. Source assessment sampling train schematic.
(Lentzen et al., 1978)

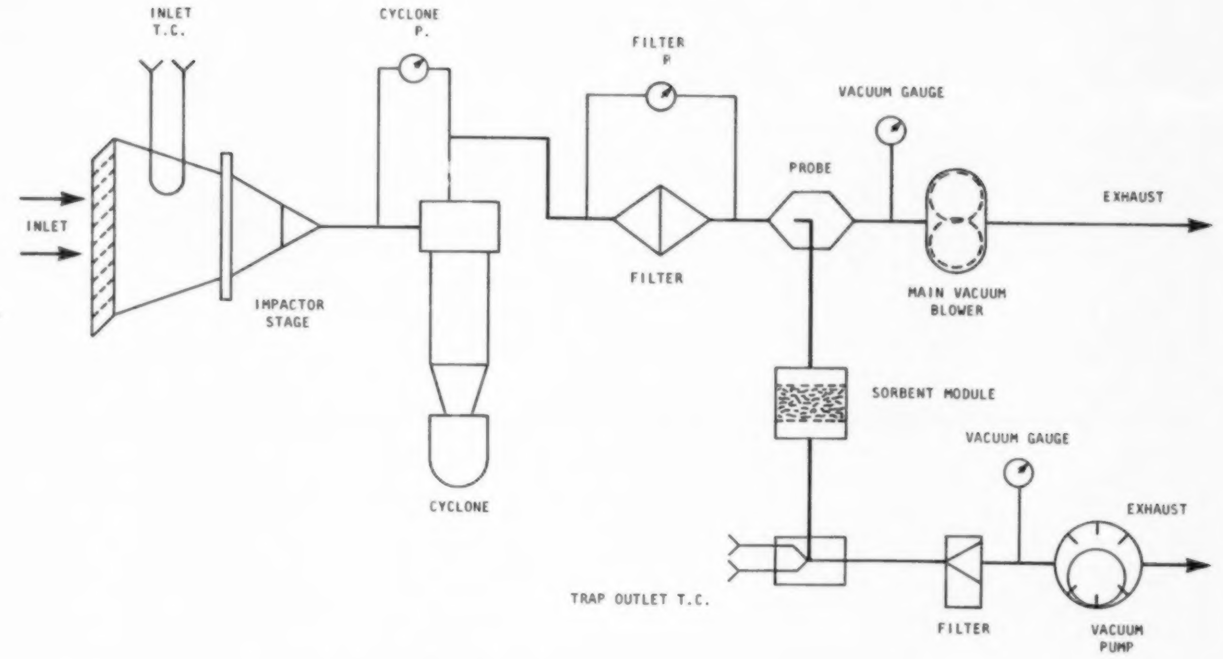

INLET T.C.
CYCLONE P.
FILTER P
VACUUM GAUGE
PROBE
EXHAUST
INLET
FILTER
IMPACTOR STAGE
MAIN VACUUM BLOWER
SORBENT MODULE
VACUUM GAUGE
CYCLONE
EXHAUST
TRAP OUTLET T.C.
FILTER
VACUUM PUMP

Figure 30. Fugitive air sampling train components.

(Lentzen et al., 1978)

the impactor was found to be unsatisfactory (Kolnsberg and Severance, 1979).

- Those between 15 microns and 3 microns (50 percent collection efficiency at 3 microns). These are collected on the cyclone. The cyclone should be adjusted to cut at 2- 1/2 microns to simulate the cut size for dichotomous samplers, but the difference is not very important for Level 1 analysis.

- Smaller particles collected on a glass fiber filter.

Organic species passing through particulate collection species that are C_6 and higher are collected on the XAD-2 sorbent module. The analysis resembles the SASS train, except that there are no impingers to collect volatile metal species (Hg, As, Sb) and enough samples to perform all biological tests may not be available. It is quite unlikely that enough hydrocarbons would be collected on the XAD-2 cartridge. AMES mutagenicity testing can be performed on 150 to 300 mg of sample, and RAM can be performed on 150 mg of sample. Determining an LD_{50} would take more sample.

According to the Level 1 manual, low molecular weight gases are to be collected in an integrated gas sampling train similar to that used to collect these species in flue gas (see Figure 31). The condenser would be needed only under extremely wet conditions, such as in a cooling tower plume.

In the absence of defined standard Level 1 procedures for these gases, the following are recommended:

- CO should be measured from the integrated gas sampling bag using the federal reference method (non-dispersive infrared analysis) or approved equivalent.

- The federal reference method (chemilluminescent), or approved equivalent, should be used to measure NO_x by sampling the air directly, not from the bag.

- Sulfur gas grab samples can be highly unstable under real ambient conditions. SO_2 should be measured by the federal reference method, or approved equivalent. Other sulfur gases should be measured using a sensitive gas chromatograph (at least 0.05 ppm sensitivity for hydrogen sulfide) with a flame photometric detector and ambient air gas sampling valve. The AID portable gas chromatograph is marginally sensitive enough for this purpose, but more stable and sensitive devices would be desirable.

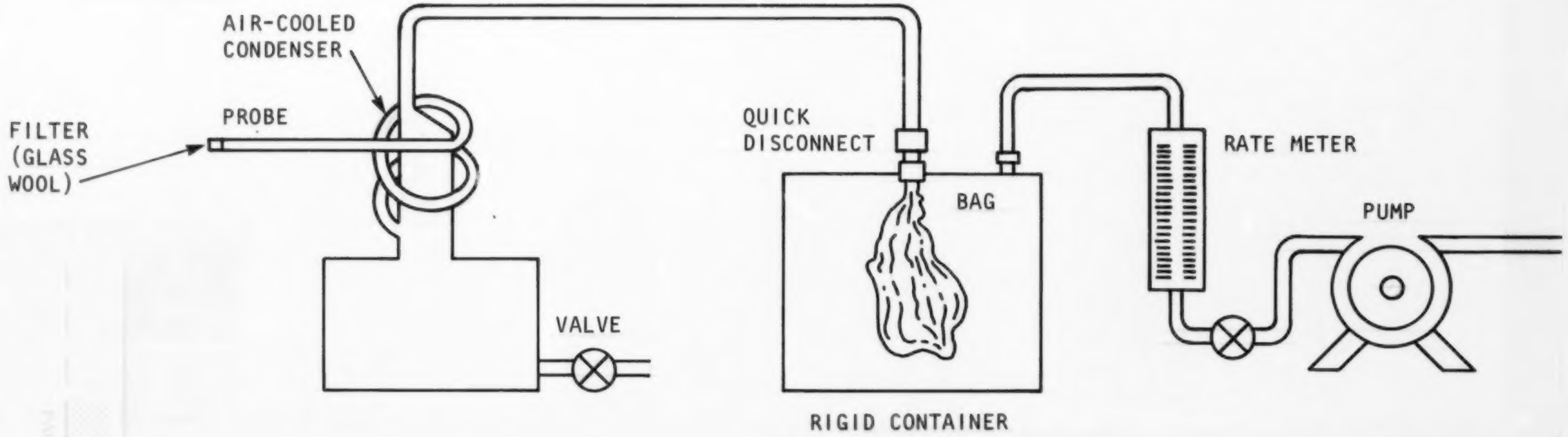

AIR-COOLED
CONDENSER
FILTER
(GLASS
WOOL)
PROBE
VALVE
QUICK
DISCONNECT
BAG
RIGID CONTAINER
RATE METER
PUMP

Figure 31. Integrated gas-sampling train.
(Lentzen et al., 1978)

- Mercury should be measured by NIOSH P and C AM Method Number 175 (National Institute for Occupational Safety and Health, 1974).
- Low molecular weight hydrocarbons should be measured by gas chromatography equipped with a Flame Ionization Detector, but the details should be researched to achieve as much sensitivity as possible for screening for substances with MEGs.

Guidance is needed on what constitutes screening procedures equivalent to Level 1/Level 2 sampling and analysis. Alternatives to the precise Industrial Environmental Research Laboratory Level 1 procedures should be acceptable, if the alternatives suggested are valid and provide at least as much useful information as the specified Level 1 procedures. Since Level 1 is designed to screen for the unexpected, alternatives should have at least as much sensitivity and accuracy for pollutant substances possibly relevant to the source that are screened for by Level 1 analysis.

Often, enough is known about the environment or process stream being sampled to justify certain types of Level 2 analysis without the need for Level 1 analysis of the parameter. Variations on the Level 1 technique may provide the necessary information at lower cost than separate Level 1 and Level 2 procedures. This is especialy true of organic analysis, where the procedures specified are expensive, and incorporation of fluorescent screening techniques and of Gas Chromatography/Mass Spectrometry analysis instead of certain portions of the Level 1 procedures may have some value under certain circumstances. Any variations should be approved by the EPA prior to implementation.

All Level 1 monitoring data should be reported into the Environmental Atmospheric Data Systems (EADS) and be systematically processed to provide upper and lower limits to the concentrations of substances with multimedia goals. When the analysis yields no information whatsoever, this should also be listed, along with the best estimate of an upper and lower limit to the concentration of the substance based on theoretical considerations (if any). The substance and the concentration range should be required inputs.

The data gathered should also be used to project peak ambient concentrations. The techniques to be used for modeling should be worked out on a case-by-case basis. Ignoring the uncertainty of the modeling, the need for further monitoring can then be priority ranked according to the uncertainty in the concentration (as a result of the limitations of Level 1 analysis)/Ambient Level Goal ratios. This priority ranking is based on ambient concentrations, but ignores the geographical extent of the problem.

Pollutants can then be selected for further monitoring based on the need to reduce the uncertainty in toxic unit discharge rates and on the need to reduce uncertainty in ambient concentration/Ambient Level Goal ratios. The need for model validation studies to reduce the uncertainty in modeling should also be considered.

Fugitive Emission Monitoring

For FBC units equipped with an effective system of hoods and fugitive air pollution control equipment, stack testing upstream and downstream of control equipment would be appropriate, using the standard stack sampling method, quasi-stack sampling method or the roof monitor method (Kolnsberg et al., 1976; Kenson and Bartlett, 1976). For installations not so equipped, and at major solid waste disposal sites, upwind/downwind testing will be necessary. The program should include testing both before and during operation of the facility.

If fugitive emissions are significant, PSD monitoring on the site may be required, including upwind/downwind monitoring.

One monitoring station should be located slightly downwind of each type of facility. For simple building geometries, and relatively flat terrain, a location two to three building heights or widths (whichever is less) downwind, along the prevailing wind direction, should be considered, and an upwind station should also be installed. The sites chosen should be undisturbed by construction and meet all site location requirements. The downwind site should be reasonably close to the ash discharge chute for truck loading, or the active portion of the landfill where FBC waste will be disposed, and within line of sight.

While only the site on the prevailing downwind side of the source usually needs to be operated on the full PSD monitoring schedule, at least four sets of upwind/downwind sampling sets employing duplicate samplers and analysis should be run, using data from a single meteorological tower with automatic wind speed and direction controlled switching equipment, or equivalent manual control. In addition to the use of a FAST train, the upwind/downwind monitoring should have:

- High volume samplers, with teflon filter pads, analyzed for sulfates, sulfites and organic adducts, along with alkalinity.
- Virtual impactor style dichotomous samplers meeting the specifications of the Office of Research and Development (Stevens and Dzubay, 1978a).

- Modified high volume samplers equipped with 4-inch (101.6-millimeter) teflon nucleopore filters with 0.4-micron pores to collect samples for automated X-ray fluorescence and electron microscopic fingerprinting of individual particles.

- Battelle ultravol 600 CFM high volume sampling for collection of enough sample for full Level 1 biological testing.

- Portable back pack samplers with silver membrane filters for X-ray defraction analysis.

The PSD site for monitoring at the location of maximum stack impact should also be included in the upwind/downwind monitoring program, providing it is in a downwind trajectory from the point source to be monitored while the fugitive emission site is also downwind. The data would be processed to determine any statistically significant differences in upwind/downwind concentrations, and the need for further monitoring would be determined.

The upwind/downwind monitoring program could be repeated for Level 2 analysis after the FBC facility and FBC waste landfill is in full operation and again a few years after the material has been permanently landfilled and the portion of the landfill being tested is no longer active. This could be used to check for off gases from bacterial action and other long-term effects.

New data gathered from pilot, demonstration or similar commercial units, and from experience with monitoring should be reviewed and used to modify this monitoring program design as necessary. An intense program such as this will not be necessary at all FBC facilities. After enough data are gathered at FBC facilities to predict impacts with reasonable accuracy, the monitoring program can be focused on those pollutants which could cause problems.

Heat of Hydration and Alkalinity--

The most important unregulated pollutant associated with FBC solid waste is calcium oxide. This is based on a comparison of projected ambient concentrations (assuming compliance of total suspended particulate levels with Class II PSD limits) with 1/420 of a Threshold Limit Value (TLV).

The only very precise technique for detecting CaO in atmospheric particulate matter is X-ray diffraction. This technique measures crystalline CaO in various states of hydration, but does not measure amorphous CaO. A review of the NIOSH computerized data base on CaO has revealed that it is significant mostly because of the heat given off when it comes into contact with water and its alkalinity. These effects may also synergize with other environmental insults to produce adverse effects. If stinging afterburn sensations are observed at locations where the general public has access downwind of an FBC facility, routine ambient air surveillance and plume transformation studies should be instituted to measure the rate of change of heat of hydration and alkalinity per microgram of sample as a function of travel time, relative humidity, and SO_2 concentrations.

Automated scanning electron microscopic and energy-dispersive X-ray fluorescence analysis may be applicable to separate the amount of particulates from the bottom ash from total ambient levels in the study. Equilibrating all samples for electron microscopic X-ray fluoresecent measurement of relative concentration of FBC waste with a humid atmosphere could be used to normalize the results. For a given mass of dry waste, they would show the same cross-sectional area and this would help in eliminating this problem for mass concentration determinations. On the other hand, separate samples, stored very dry and introduced directly into the electron microscope immediately after analysis, could provide some information on the rate of hydration of the particles by examining their "puffiness" through morphological identification of how expanded the particles are.

The first few heat of hydration tests should be performed on the fugitive dust emitted when the bottom ash is emptied directly from the boiler to the hopper, collected while it is still hot, if possible. The sample should be of minimum size to eliminate spontaneous hydration during sampling, and it should be segregated by particle size. Crushable filters are preferred for heat of hydration measurements. The heat of hydration of the particles collected should be measured with a sensitive microcalorimeter with dual cells (one for a blank filter and water capsule, and one with an exposed filter and water capsule), with plungers to facilitate breaking the capsules. Sensitivities for heat of hydration of a few microcalories can be obtained using available state-of-the-art equipment. Marche Instruments, Inc., in Lyon, France, and possibly Tronac (Orem, Utah) manufacture instrumentation and measurement cells. Blank filters should be run to test the amount of uncertainty in the zero heat of hydration measurements. If the heat of hydration of the fresh bottom ash fugitive particulates is appreciable, methods should be developed for ambient air analysis for heat of hydration. Plume transformation and particle size and deposition-related studies should be performed to determine how far downwind this effect could have significant impacts, as a function of environmental conditions and emission rates. The main potential problem is hydration of particles collected on the filter or in the sampler while air is passed over them during the process of collection. An ambient sampler that dilutes the sample with ultra-dry air before collection might help; another approach is to create a wet filter medium impregnated with pigments that permanently change color when a certain temperature is exceeded. Spots on the filter would be a crude index for the number of particles having an appreciable heat of hydration.

The heat of hydration of the particulates from the spent bed material can combine with the alkalinity to produce sensations similar to being "bit" by the dust, with an alkaline afterburn. A program of skin sensitivity testing could be established, utilizing varying doses of FBC spent bed material with varying documented heats of hydration, surface temperatures during hydration, alkalinity and size. Similar-appearing inert material would be needed as a control, and the program should be performed using double blind experimental procedures. The chromium content of the dose would also be measured, and the locations where doses were administered would be examined for surface skin allergic reaction or any damage a few days after testing. Effects on vegetation, scratched and unscratched paint panels and other sensitive receivers should also be studied. The end point of this research would be to determine ambient goals for these parameters based on health effects, ecological effects (including property damage), and nuisance value. The research could also be used in the design of monitoring programs. Pigments in impregnated filters set to change color at temperatures and heat inputs similar to those that cause adverse impacts could be designed, based on the results of the program. The necessary sensitivity and other details for calorimetric experiments could also be determined.

Portable Wind Tunnel Monitoring--

Midwest Research Institute has developed a new and definitive method of studying emission rates from aggregate storage piles and landfills. A portable wind tunnel, with an open bottom and skirts (to seal the open area around the edges) is placed over the surface to be tested. High volume isokinetic samples are taken with a cascade impactor equipped stack test train as the tunnel is operated at different velocities (Coherd and Cuscino, 1979).

The technique brings out certain features of the behavior of windblown dust emissions in a more direct and cost-effective manner than upwind/downwind sampling. It easily generates information on:

- The threshold velocity for the onset of wind erosion on crusted and uncrusted surfaces for different particle sizes

- The dependence of the emission rate on wind velocity

- The rate of decrease of emission rates from surfaces when exposed to a constant wind velocity

Emission rates, however, are not completely uniform over material pile surfaces. Rates vary with the wind velocity and the properties of the surface. Measurements of the wind field close to the surface of a pile (or a simulated pile in a wind tunnel or theoretical model), combined with information on the amount of crusted, aged, and disturbed surface area, and the results of field testing with the wind tunnel, would have to be combined to obtain an accurate estimate of the total mass emission rate for the pile, using the portable wind tunnel technique. Research is underway to develop cost-effective techniques to do this and to compare the results to upwind/downwind monitoring. The technique is also not applicable to measuring emission rates from portions of a pile being actively worked. This technique should be considered for detailed studies of windblown dust from raw material and solid waste piles associated with FBC processes. The results of such testing could also be used to determine at what wind velocities it might be appropriate to perform upwind/downwind testing of emission rates and to generate those emission rates, once suitable techniques for simulating wind fields and making the necessary calculations are validated in field tests. When the technique is used, it is suggested that the runs be made on the following types of surfaces:

- fresh dry surface

- crusted dry surface, both disturbed and undisturbed

- wet surface, both disturbed and undisturbed

- aged weathered crusted surface, both disturbed and undisturbed.

Replicate runs on different portions of the same type of surface should be performed to measure precision. The use of the EPA high volume Level 1 SASS train, in combination with the wind tunnel, should also be considered.

Sulfates, Sulfites and Organic Adduct Analysis--

There are varying methods for measuring sulfates and sulfites (Hansen et al., 1976). The EPA routinely uses boiling water extractions and the methyl thymol blue method (or the "thorin" method) to measure sulfates on high volume sampler filters and ion chromatography; and a cold water extraction procedure to measure sulfate and sulfite on dichotomous samples (Stevens and Dzubay, 1978a) and during Level 1 analysis (Lentzen et al., 1978). The ion chromatograph is calibrated against known sulfate and sulfite solutions. X-ray fluorescence analysis of sulfur was shown to give reasonably consistent results, when compared to the ion chromatographic analysis of sulfates, for typical ambient dichotomous samples, if the sulfur on the filter is assumed to be sulfate. X-ray fluorescence may also be used to measure sulfates in the ambient air. Measurements of ammonium and hydrogen ions suggest that the sulfate is usually in the form of ammonium sulfate. EPA-sponsored analysis of ambient samples by ESCA X-ray photoelectron spectroscopy also has shown the sulfur to be in the form of sulfates (Stevens and Dzubay, 1978b).

In an alternative technique, sulfur (IV) is measured by thermometric titration with $K_2Cr_2O_7$, followed by the determination of sulfate by $BaCl_2$ titration (Hansen et al., 1976). This technique reputedly measures true sulfate, while the hot water extraction technique converts other sulfur species to sulfates, resulting in less accurate determinations. Evidence suggests that the ion chromatrographic technique is subject to interference because of the conversion of S (IV) to sulfates during the alkaline phase of the analysis because of the catalytic activity of Fe(III) and Cu(II) (Eatough, 1979). Hansen et al. (1976) and Eatough (1979), using Electron Spectroscopy for Chemical Analysis (ESCA), also demonstrated the presence of sulfate and sulfite in some samples. For smelters, sulfate plus sulfite by the thermometric method is often less than half the sulfate measured by approved EPA methods. For power plant plumes, thermometric sulfate may sometimes be half the sulfate measured by EPA methods. For typical ambient air the difference may only be 10 percent.

There is evidence suggesting that organic adducts of sulfur change to inorganic sulfates if the sample ages for a week. Significant conversion can even occur overnight (Eatough, 1979). As a result, sulfur species analysis should be performed immediately after sampling in the field. Evidence exists suggesting that these sulfur (IV) species and organic adducts form in power plant plumes downwind (Eatough, 1979) and that some of the organic adducts such as monomethyl sulfate and dimethyl sulfate are mutagenic and carcinogenic (Druckrey, et al., 1966). The formation of inorganic sulfur (IV) may be promoted by moisture, soluble iron or copper, and relatively low acidity. These properties of the FBC flue gas particulates should be measured and compared to the particles from conventional boilers.

A method needs to be developed for preparing stable sulfate, sulfite sulfur and organic adduct of sulfur compound standards in matrices similar to fly ash, coal, limestone, and urban dust, on filters stored cryogenically with different reactive components micro-encapsulated. National Bureau of Standards might help to referee tests, establishing such a method through collaborative testing of NBS audit samples by the EPA, the Electric Power Research Institute and the U.S. Department of Energy contractors and in-house labs. Samples would contain varying (but known) amounts of sulfates, sulfites, sulfides, elemental sulfur and organic adducts on matrices simulating environmental samples (with substances that may cause interference). Naturally, the stability of the samples and sample handling procedures would have to be established prior to the collaborative testing, and the parties analyzing the samples (outside NBS) would not know the content before analysis and data reporting.

In the absence of sulfate, sulfite and organic adduct standards, it is still possible to test how well the various techniques measure sulfates in isolation. The recent National Bureau of Standards Standard Reference Material 2673 prescribes three pairs of strips of fiberglass high volume filter with known sulfate content and two blank filters. The techniques should be calibrated by the usual methods, the NBS filters should be analyzed, and NBS concentration compared to the measured concentrations.

Another type of test to resolve the problem would be to take ambient high volume samples in a power plant plume, split the sample into four equivalent strips, and spike two of them with equivalent known amounts of sulfites (preferably Fe S and other species found in ambient air). The differences between the spiked and unspiked samples could then be processed, along with the amounts of sulfites added, using standard statistical techniques, to yield information on the recovery of sulfites and on the error in the measurements. The experiment could be repeated with sulfate spiking, organic adduct spiking, and sulfide spiking. Care must be taken that the spiked substance is not converted to other materials because of interaction with the collected particulates before analysis begins.

If the thermometric technique gives consistent results when compared to NBS sulfate standards and EPA quality assurance sulfate samples, serious consideration should be given to measuring equivalent sulfates and sulfites by both the standard EPA techniques and thermometric techniques in FBC testing programs. Ideally, both techniques should be performed in the field immediately after sampling. A portion of the solution used for thermal analysis should be aged for a few days and differences in the Fe S(IV) species concentrations as a result of this aging can be used to measure total organic adducts (Eatough, 1979). The thermal technique requires at least 2 to 4 mg of sample; therefore, it is suitable for samples from FAST trains and high volume samplers, but unsuitable for most dichotomous samples. For accurate analysis, samples larger than 2 to 4 mg are recommended.

Polynuclear aromatic hydrocarbons and polar and non-polar organic and inorganic mutagens have been observed on fly ash surfaces from conventional power plants (Fisher et al., 1978). Available information on FBC shows very low levels of polynuclear aeromatic hydrocarbons, but the material is mutagenic, according to AMES testing (Murthy et al., 1977). Recent research shows dimethyl sulfate and monomethyl sulfate at concentrations as high as 830 ppm in fly ash and airborne particulate matter from conventional coal combustion processes (Lee et al., 1979). These substances may be, in part, responsible for the observed mutagenicity of fly ash because these substances have proven mutagenic and carcinogenic properties (Druckrey et al., 1966; Druckrey et al., 1970; Couch et al., 1978). The available data base should be examined to create zero threshold MEGs for these substances. Testing should be considered in FBC effluent and FBC plumes, if the polar organic fractions of the solid waste and fly ash are found to be mutagenic.

To measure dimethyl sulfate in the ambient environment, an acid washed high volume sampler filter is used to collect at least 20 mg of sample (preferably more). It is extracted with methanol and analyzed by ion chromatography. The material is believed to oxidize to sulfate in the ion chromatograph, so the method gives a lower limit to concentrations. Dimethyl sulfate is measured by gas chromatography/mass spectroscopy (GC/MS) (Lee et al., 1979).

Long-Range Plume Transformation Studies--

One of the important impacts of SO_2 emissions is the eventual formation of acid rain and sulfates downwind of the source. Several monitoring programs are being performed to study this phenomenon for conventional power plants. They include:

- Multistate Atmospheric Power Production Study (MAPPS), sponsored by the U.S. Department of Energy
- Sulfur Transport and Transformation in the Environment (STATE), sponsored by the U.S. Environmental Protection Agency
- Major studies in Europe and Canada
- Studies by the Electric Power Research Institute

The usual rate of sulfur dioxide oxidation observed in relatively clean surroundings is less than five percent per hour, although higher rates are occasionally reported. Therefore plume transformation studies are usually performed at large, isolated plants, to facilitate separation of a plume from background levels after it has traveled for many hours downwind. The techniques in these studies do not yield important information on the oxidation rate of SO_2 from FBC units unless the unit is:

- Isolated from other boilers during the test
- At least 200 megawatts in size or has very high SO_2 emission

Short-Range Plume Transformation Studies--

Physical and chemical changes often occur in effluents after they have been emitted to the atmosphere. As hot flue gas and particulates exit a smoke stack and rapidly cool, fumes may condense and the chemical composition of the effluent may change. Portable stack test trains should be developed that dilute and cool flue gas with clean cool air and allow a reasonable amount of residence time for the material to establish chemical and physical equilibrium before analysis. A low volume dilution stack test train could be useful for collecting particulate samples for automatic electron microscopic/X-ray fluorescent "fingerprinting". This would aid in their positive identification and separation from total suspended particulate levels downwind in ambient monitoring programs. Comparison of diluted and undiluted particulate size distribution and morphology would also help in determining whether fumes could cause significant plume opacities not measured inside a stack.

Balloon Borne Sampling System--

The Denver Research Institute has developed a lightweight battery-operated balloon borne sampler that is small enough not to require an FAA license for operation. As Figure 32 illustrates, it consists of eight remotely controlled, individually selected filters, gas sampling tubes, a pump, dry and wet bulb temperature telemetry, and a lightweight plume detector with telemetry. The sensor detects at least methane, carbon monoxide and isobutane. The device can also be used to fill sample bags. Currently being tested at conventional power plants, its use for FBC should be given serious consideration. Particle samples could be taken within and outside the plume, and analyzed by automated scanning electron microscopy with X-ray fluorescence detection. The source "fingerprint" obtained in this manner could then be compared to that measured by more conventional extractive stack testing, and any differences noted. If the projected cross-sectional area size distribution of the particles

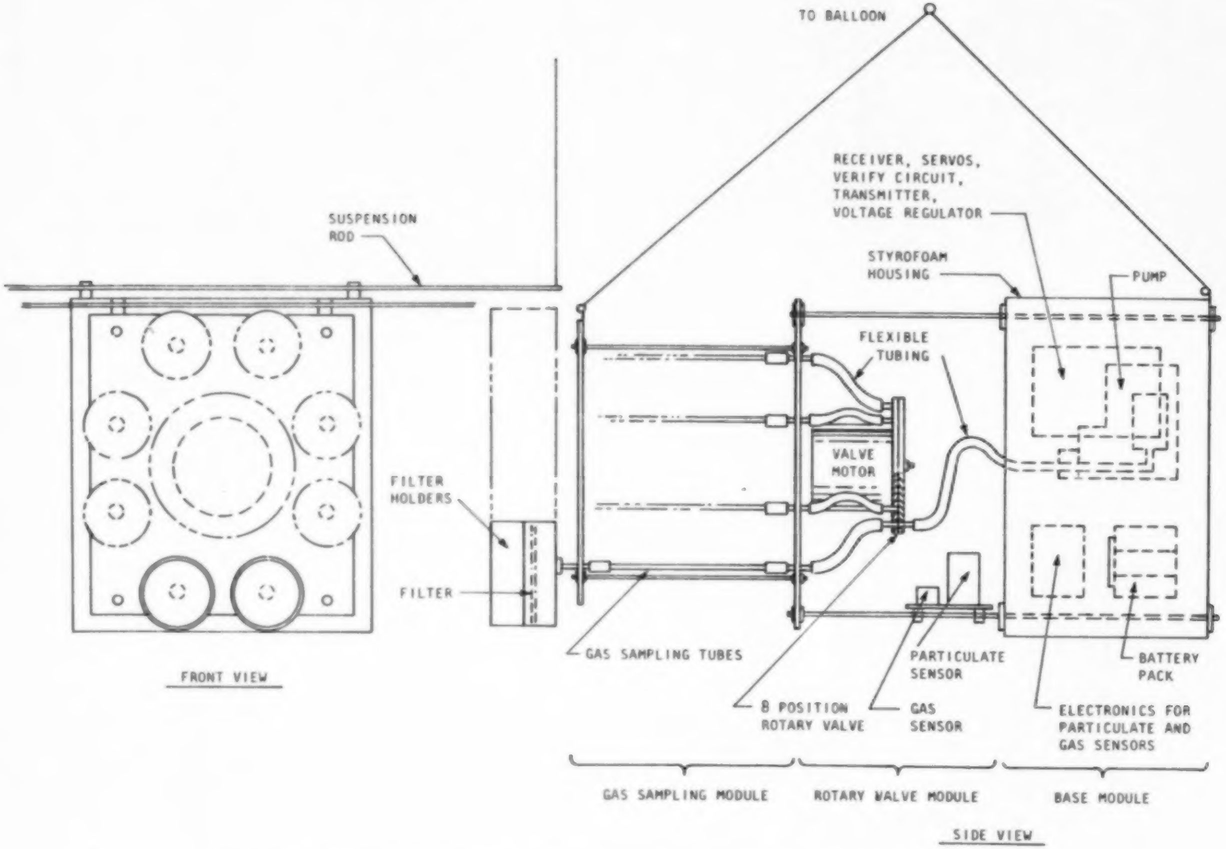

TO BALLOON
RECEIVER, SERVOS, VERIFY CIRCUIT, TRANSMITTER, VOLTAGE REGULATOR
STYROFOAM HOUSING
PUMP
SUSPENSION ROD
FLEXIBLE TUBING
VALVE MOTOR
FILTER HOLDERS
FILTER
GAS SAMPLING TUBES
PARTICULATE SENSOR
BATTERY PACK
8 POSITION ROTARY VALVE
GAS SENSOR
ELECTRONICS FOR PARTICULATE AND GAS SENSORS
GAS SAMPLING MODULE
ROTARY WALVE MODULE
BASE MODULE
FRONT VIEW
SIDE VIEW

Figure 32. Schematic of second generation sampling package.

(Denver Research Institute, 1979)

changes appreciably between in-stack measurements and out of stack measurements, the implications on plume opacity should be derived. Attention should be given to any evidence of fume condensation in the morphological analysis.

The SO_2 is measured in gas sampling tubes or on impregnated filters, and the particulate concentration is determined by weighing the filter and automatic electron microscopy, the ratio of concentrations (after subtracting background levels) can be compared to those measured within the stack. If they are within acceptable limits, the method has some value for roughly estimating particulate emission rates. The ratio of Total Suspended Particulates (TSP) to SO_2 concentrations could be multiplied by the SO_2 emission rate to estimate emission rates. The ratio of concentrations could even be multiplied by the in-stack SO_2 concentration to estimate the particulate concentration in the stack, providing fume condensation and secondary particle formation are not significant. The values thus derived could be compared to those indicative of compliance with regulations. If CO_2 were measured in the gas sampling tube (and upwind), the results could be converted to emissions.

The balloon-borne system can be modified by attaching a gas sampling bag on the pump exhaust. Fewer particulate and gas samplers could be used at the pump inlet to compensate for the weight of the bag. When used upwind and downwind from the source, the amounts of particulates, SO_2 , and CO_2 caused by the source could be estimated. These data would then be processed to determine emissions in the same way that it is done in the stack. The system is currently being tested for the quantitative measurement of sulfates, and sulfuric acid mist; it may prove to be applicable to FBC.

A modification of the balloon borne sampling system is under consideration for collecting samples for biological testing. Samples would have to be collected over a number of days to obtain enough samples for even simple AMES testing. When tethered balloons are used, attention must be given to power lines and to the stability and suitability of meteorological conditions.

Larger samples could be obtained over a short period of time by hoisting high-volume samplers, FAST samplers or Battelle ultravol samplers into plumes with aircraft, cranes, meteorological towers or by placing them on strategically located buildings.

Opacity Measurements

The opacity caused by water droplets is generally excluded from the regulations, except for some local ordinances aimed at eliminating hazardous driving conditions on public roads caused by fog from man-made moisture plumes.

Opacity Mass Concentration Relationship--

Plume opacity is related to the particular mass concentration by the Beer-Lambert Law (Ensor and Pilat, 1970):

$$I/I_o = e^{-\left(\frac{W\,L}{K\,p}\right)} \tag{21}$$

Where:

Opacity = $1 - \frac{I}{I_o}$ = the fraction of a light beam incident on a plume that is scattered or absorbed

I = the intensity of that portion of a light beam transmitted through a plume without being scattered or absorbed

I_o = the intensity of a light beam before passing through a plume

W = the particulate mass concentration (g/m^3)

L = the total distance over which the opacity is measured (in meters)

K = the specific particulate volume/light extinction coefficient ratio (cm^3/M^2)

p = the density of the particles in the plume (g/cm^3)

Ensor and Pilat (1970; 1971a and 1971b) have published computerized graphs showing the value of K versus the geometric mass mean radius for spherical particles with a uniform density and log-normal size distributions (Figure 33). Several curves are drawn on each graph, each corresponding to different standard geometric deviations of the particle radius. Each graph corresponds to a given wave length of light and refractive index. Several conclusions can be made from these curves:

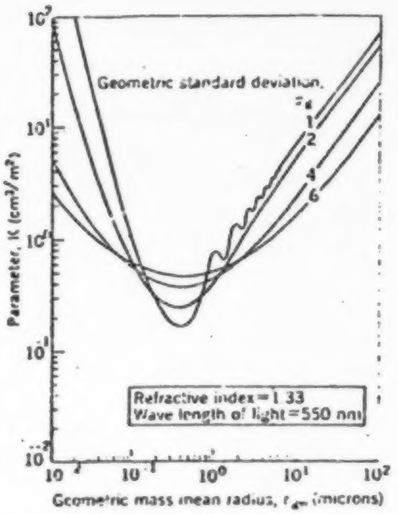


Figure . Parameter K as a function of the log-normal size distribution parameters for id water.

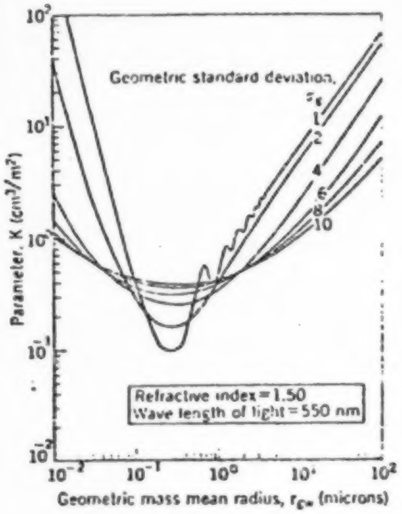


Figure Parameter K as a function of the log-normal size distribution parameters for a white aerosol.

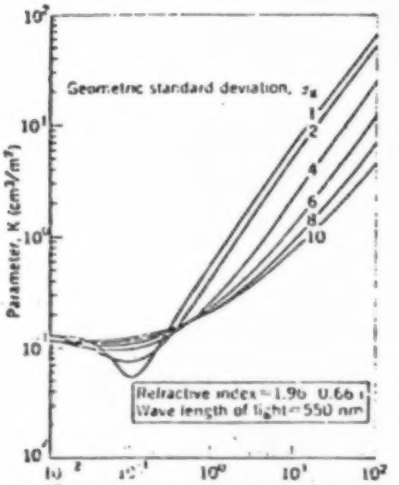


Figure Parameter K as a function of the log-normal size distribution parameters for a black aerosol.

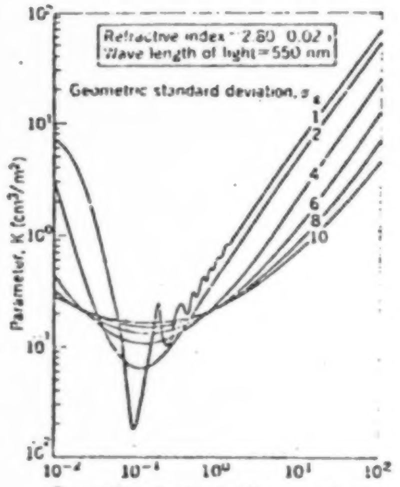


Figure Parameter K as a function of the hypothetical refractive index for iron oxide.

Figure 33. K as a function of log normal size distribution parameters. (Ensor and Pilat, 1971a)

- The magnitude of K is critically dependent on the particle size distribution.

- The particle refractive above a geometric mean radius equal to twice the wave length of the incident light index does not significantly influence the plume opacity. For particle sizes near to and below the wave length of light, the refractive index is a significant variable.

- Variations in the wave length of light do not cause large variations in K for particles much larger than the wave length of light.

- K becomes increasingly insensitive to changes in the size distribution for polydisperse aerosols with diameters near the wave length of light.

A proportion of particles from FBC is irregular. Preliminary testing with a dilution stack test train and photomicroscopy shows very few spherical particles for the U.S. Department of Energy Morgantown FBC (Carpenter et al., 1978), suggesting that the effect of fume condensation on opacity is likely to be negligible. For these particles, the concept of a single particle radius breaks down, and the type of radius that has been found to be most useful in light scattering calculations is the radius of a circle with the same area as the projected cross-sectional area of the particle, averaged over all possible particle orientations. For highly irregular particles (such as fibers), with dimensions near to or smaller than the wave length of light, K can be sensitive to the particle shape.

When the specific particulate volume/light extinction coefficient ratio (K) of the particles in a plume and the density of the particles are stable, the mass concentration of the particles in the plume may be monitored by measuring the opacity of the plume across a measured distance. This can be accomplished by solving the Beer-Lambert Law for the particulate mass concentration (W):

$$W = -\frac{p\ K\ (\ln(I/I_o)}{L} \qquad (22)$$

When considering the application of this equation to combustion sources, it is important to differentiate between dust, smoke and fumes (White, 1968):

Dust is formed by the pulverization or mechanical disintegration of solid matter into particles of small size

> by such processes as grinding, crushing, blasting, and drilling. Particle sizes of dust range from a lower limit of about 1 micron up to about 100 or 200 microns. Larger particles, although formed, settle too rapidly to remain in suspension an appreciable time. Dust particles are usually irregular in shape, and particle size refers to some average dimension for any given particle. Common examples of dusts are fly ash, rock dusts, and ordinary flour . . .
>
> Smoke implies a certain degree of optical density and is derived from the burning of organic materials such as wood, coal, and tobacco. Smoke particles are very fine, ranging from less than .01 micron up to 1 micron. Smoke particles are spherical in shape if of liquid or tarry composition such as tobacco smoke, and irregular if of solid composition such as soot or carbon black . . .
>
> Fumes are formed by processes such as sublimation, condensation, or combustion, generally at relatively high temperatures. Perhaps the commonest fumes are derived from the oxidation of metallic vapors or compounds, e.g., lead oxide fume . . . Fumes range in particle size from about 0.1 micron to 1 micron . . .

When the size distribution of the smoke, fumes and dust associated with a combustion operation are constant, there will be a characteristic P times K value associated with each component of the plume. The transmittance of the plume (I/I_0) is the transmittance of the smoke component multiplied by the transmittance of the fume component multiplied by the transmittance of the dust component. Small particles (smoke and fumes) can be expected to usually have smaller K's than dust particles, when measured at wave lengths in the visible region (0.4-0.7 microns). For particles with smaller K's, smaller amounts of mass will produce the same opacity. Thus, the ability of a given mass of smoke or fumes to produce a given opacity in the visible region is usually greater than for dust. If a stable relationship between mass concentration and opacity is to be found for a source emitting smoke, fumes, and dust, the following factors must be present:

- Either two of the three components have optically negligible effects on opacity
- The volume fractions of the components are stable
- The Ks of the components are nearly equal

Data accumulated in Germany indicate that fly ash concentrations from some pulverized coal-fired power plants may be monitored by plume opacity measurements with a 95 percent confidence of being within about ±30 percent of the actual in-stack mass concentration (determined by isokenetic sampling), except during periods of soot blowing (Buenter, H.P., Lear Siegler, Inc., to Cornett, C.L., personal communication).

Special Considerations for FBC Units--

Particles from chemically active FBC units are mostly unfused. This makes the size of the flue gas particles more dependent on the physical coal characteristics than conventional pulverized coal-fired boilers. This would cause a less stable relationship between particulate mass concentration and plume opacity than for pulverized coal-fired boilers. Nevertheless, with emission limitations requiring a 99 percent efficiency of collection of particulates, and EPA's plans to regulate inhalable particulates, it would be worthwhile to investigate the relationship between plume opacity and particulate mass concentration for FBC units and associated equipment (coal and limestone preparation plants, solid waste transfer and disposal operations, etc.).

Many series of simultaneous mass concentration and plume opacity measurements need to be made for a broad range of process variations using a variety of coals to study K x P patterns for the technology as a whole. Studies at single installations over a long period of time could help determine the applicability and limitations of such optical monitoring at individual sources.

Applications of Opacity/Mass Concentration Relationships--

Air pollution control agencies in Germany require empirical calibrations of the relationship between particulate mass concentration and plume opacity for large pulverized fuel fired installations. Based on such calibrations and process related information (such as the relationship between mass concentration and pounds of emissions per million Btu or other relationships that can be related to standards), individual plume opacity standards are being set which serve to automatically enforce appropriate mass concentration limits for such sources (Peeler, 1979).

If the relationship is determined downstream of pollution control equipment, and the equipment breaks down, the relative large particulate concentration usually is enhanced. This often causes the opacity/mass concentration calibration, when control equipment is working, to underestimate the true particulate concentration. If the opacity implies violation of standards under these circumstances, the exceedance is greater than implied by opacity.

Ratios of average concentrations of particulates to CO_2 concentrations or of particulate to CO_2 emission rates are routinely used to measure emissions. Upper limits to CO_2 concentrations for flue gas from a boiler can be used to establish upper limits to the particulate concentration. If particular emissions are related to opacity in a known manner, it should then be possible to establish upper limits to opacity indicative of compliance with standards. Oxygen monitoring of the flue gas may also be used to measure combustion efficiency. The continuous monitoring of oxygen or CO_2 content of flue gas from federally regulated FBC units is required to help process SO_2 monitoring data to determine compliance with regulations. Both types of monitoring suffer from interference from the limestone. Estimated mass concentrations from opacity measurements could be processed in a manner similar to the processing of SO_2 concentration measurements to derive information on compliance with emission standards.

If the relationship between opacity and compliance is known, along with the errors, but the results are not considered conclusive, opacity might be used to show probable cause for suspecting a source to be not in compliance and to obtain entry warrants and dispatch a stack test team for accurate measurements.

Continuous records of plume opacity before, during, and after stack testing can also be used to indicate if conditions during stack testing represent normal operating conditions.

Transmissometers are also often used as "broken bag detectors" for baghouses. The sensitivity of such devices to particulate mass loadings from FBC units needs to be determined, along with the amount of uncertainty in the relationship.

If the relationship between particulate concentration and opacity is stable, opacity monitoring could be combined with monitoring the total volume rate of flow out the stack to yield an estimate of the total particulate emission rate. This emission rate could be compared with the maximum allowable, when the installation is operating at full capacity. Exceedances of the maximum allowable emissions (with a reasonable margin determined by the stability of the opacity/mass concentration relationship) could indicate non-compliance with emission regulations. Laser anemometers or the Visiplume SO_2 television remote sensor (Exton, 1977) could be used to measure average velocities remotely, when applicable. These velocities can be combined with the dimensions of the stack mouth to calculate the volume rate of flow out of the stack.

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In-Stack Opacity Measurement--

For those sources with in-stack transmissometers already installed, the existing equipment should be used, providing they:

- Meet specifications and are properly installed, operated, and maintained.
- Have an acceptable history of low zero and span drift at the actual installation

A long-term program of stack testing should have a permanently installed transmissometer. When this is not practical or cost-effective, a portable transmissometer with a stack test probe should be used where applicable. Care should be taken, however, to clean the stack sampling port before inserting the probe, especially for units under considerable negative pressure, because dirt can contaminate the optics when the probe is inserted or during operation. Random drift of instrument response due to thermal expansion can be avoided by allowing the in-stack probe to come to thermal equilibrium. The device should also have suitable structural design and integrity to withstand both the air flow conditions and temperature of the plume without damage or calibration drift. Units that have proven their accuracy against permanently mounted transmissometers at boiler installations are preferred. Compressed air should be used, when ecessary, to keep the optics clean throughout the test period and to confine the plume to a measurement slot of known length.

The opacity should be recorded continuously, and translated into an average value of $\ln (I/I_O)$ during the time period of the particulate sampling. Automatic equipment is available for this purpose. The distance over which the opacity was monitored, the particulate mass concentration, the location where opacity and mass concentration was measured, and appropriate process data to translate the concentration into terms comparable with regulations, should also be recorded.

Some information about the potential variability of K can be obtained by calculating K from measured particulate size distributions, particularly if cut sizes less than 0.5 micron are included. (See Figure 33 for size distributions that are approximately log normal.) Aerodynamic size distributions can be of some value in such studies although projected cross-sectional size distributions are preferred.

If there are no visible emissions, transmissometers in this effluent may not yield useful information and may not be appropriate (except as an indicator of non-control if there is

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an appreciable opacity upstream of control equipment), unless the equipment is extremely sensitive. Opacity monitoring would not be appropriate in wet plumes (plumes containing enough uncombined water as to cause an appreciable opacity compared to that of the pollutants in it), unless the purpose is to measure the water droplet concentration.

Remote Measurement of Plume Opacity--

Trained Observers--Plume opacity can also be measured outside smokestacks. EPA Method 9 involves the use of trained observers to measure the plume opacity by its appearance. The procedure contains detailed procedures for the training and certification of observers every 6 months and procedures to be used in field tests. When the plume does not contrast well against the background, the method can result in gross underestimates of opacity. Under contrasting conditions, field experiments indicate that 99 percent of Method 9 determinations were no more than 5 percent above the results of in-stack measurements for black plumes and no more than 7.5 percent of in-stack measurements for white plumes. The accuracy of local smoke inspectors could be different and should be periodically audited.

Auditing the accuracy of certified smoke inspectors by researchers at Rutgers University, using standard smoke generators and EPA Method 9 testing procedures, showed that only 40 percent of the inspectors could pass all criteria for certification at least 6 months after their last certification. Average errors for white smoke were 6.2 percent; for black smoke, the average error was 5.5 percent. Some inspectors did twice as well as this and some were twice as bad. Errors above 15 percent occurred about 3.6 percent of the time for white smoke and 2.4 percent for black smoke. Some inspectors erred by this much about 10 times as often as the average.

Data on secondary aerosol formation (fume condensation) in fluidized bed boiler flue gas should be gathered to determine if such particulates could have an appreciable opacity which could influence the relationship between in-stack and out-of-stack measurements. The use of stack sampling trains that dilute the particles with cool air before collection, along with conventional samplers, could be useful for checking for such aerosols. Ambient plume sampling could also be used. The projected cross-sectional area size distribution of the particles in the plume after cooling should be contrasted to that of the particles at stack temperature for this purpose. Fume particulates tend to be spherical.

When changes in particulate size distribution are negligible, out-of-stack measurements of opacity can be used as a quality assurance auditing procedure for in-stack opacity measurements (considering the errors in such measurements). EPA Method 9 could be used during the daytime to check for gross in-stack measurement errors. The remote measurements are valuable because regulations cover out-of-stack opacity not caused by water.

The Method of Contrasting Targets--The successful application of photographic and telephotometric techniques to the measurement of plume opacities has been documented (Conner and Hodkinson, 1972). This was accomplished by measuring the difference in the apparent luminances of contrasting targets when seen through a plume ($B'_1 - B'_2$), and the apparent difference in luminances of these targets when seen clear of the plume ($B_1 - B_2$). The transmittance, T ($=I/I_o$), of the plume is calculated from the relationship:

$$T = \frac{B'_1 - B'_2}{B_1 - B_2} \tag{23}$$

The relative luminances of the targets may be obtained with direct telephotometer measurements, or by photographing the targets and obtaining the measurements from the negative in a laboratory using a densitometer. A high quality camera should be used to minimize changes in the relative luminance calibration across the negative or photographic plate. Neutral density filters are positioned along the film plane to produce a calibration scale on the negative.

Telephotometer measurements of plume opacity, using the method of contrasting targets, yielded results which were within, on the average, 4 percent of the opacity of a white experimental plume as measured in the stack (Conner and Hodkinson, 1972). The agreement between the in-stack and out-of-stack opacity measurements was within the range of random experimental error and differences between the wave length dependent light energy response of the devices. The photographic method also showed promising results.

Laser Radar--Laser radar may be used to measure plume opacity during day and night. This technique works by measuring the amount of backscatter of light (normalized for the response characteristics of the laser radar with distance) from particles in front of the plume (I_o) to the backscatter from the particles behind the plume (I). Opacity is $1-I/I_o$. Preliminary indications are that it is accurate to within ± 3 percent to ± 6 percent of in-stack measurements (Dybdahl and Cunningham, 1979). Inhomogeneous background concentrations of particles near the plume in heavily polluted environments can sometimes cause greater (up to 12 percent) errors (Conner, 1979).

Laser radar is especially useful at night, when other less exotic techniques of opacity measurement (except for in-stack measurement) are not applicable. The National Enforcement Investigations Center (Denver, Colorado) laser radar unit has proven to be useful in enforcement-related activities. It can be dispatched for surveillance of sources suspected of "dumping at night" or falsifying in-stack opacity measurements. Most laser radar units usually measure plume opacity at one wave length only, rather than across a range of wave lengths. This can cause the raw readings to be up to 50 percent lower when opacity is dominated by submicron particles for some laser radar units, especially for particles less than the wavelength of light in size (Conner, 1979). There are simple visual checks for submicron particles--plumes with opacities dominated by very small particles tend to appear blue and cast red shadows. It is possible to correct for the spectral response of a laser radar using sun photometers to measure the wavelength dependence of the extinction coefficient (Conner, 1979). Multiple wavelength laser radar units are also being developed to measure opacity and to give some information on particulate size distribution.

Sun Photometer--Opacity can also be measured by measuring the intensity of light from the sun when viewed through a plume and clear of the plume. The angle viewed through the plume should also be considered, since opacity measurements should reflect measurements perpendicular to the plume axis.

DATA REPORTING

The results of all FBC monitoring programs should be reported to 1) the permit-granting authority for the facility tested, 2) the EPA Industrial Environmental Research Laboratory, 3) EADS computerized data bank, (when it is ready to accept data) and 4) to the EPA Regional office, if required. The data should also be sent to:

U.S. Environmental Protection Agency Advanced Process Branch
Industrial Environmental Research Laboratory
Research Triangle Park, North Carolina 27711
(919) 541-2825

The results of any programs comparing the results of in-stack monitoring against those of non-intrusive methods should be reported to:

U.S. Environmental Protection Agency Quality Assurance Division
Research Triangle Park, North Carolina 27711
(919) 541-2580

and

U.S. Environmental Protection Agency Emission Measurement
  and Characterization Division
Mail Drop 46
Research Triangle Park, North Carolina 27711
(919) 541-3034

The results of opacity measurement programs (and the methods of testing used) should be reported to:

U.S. Environmental Protection Agency Emission Measurement
  and Characterization Division
Stationary Source Emission Measurement Research Branch
Mail Drop 46
Research Triangle Park, North Carolina
(919) 541-3173

Technical Coordinator
Technical Support Branch
U.S. Environmental Protection Agency Division of Stationary Source Enforcement
Mail Drop 7
Research Triangle Park, North Carolina 27711
(919) 541-4571

SECTION 5

WATER QUALITY MONITORING STRATEGIES

INTRODUCTION

FBC of coal is a fossil fuel combustion technology that, in respect to the emission of water pollutants, is similar to those from conventional pulverized coal combustion plants. Conventional pulverized coal combustion plants which burn high-sulfur coal are required to use some form of flue gas desulfurization to remove the sulfur dioxide prior to discharge of the gaseous emissions to the atmosphere. Many of the flue gas desulfurization techniques produce an aqueous mixture or sludge as the waste product which must be disposed of in a landfill or by other methods. FBC technology, on the other hand, removes the sulfur dioxide at its source, producing only solid wastes, and therefore has no aqueous or liquid effluents associated directly with the technology.

The use of FBC technology for commercial purposes would, of course, require other processes such as steam generation and water cooling. The aqueous discharges associated with the use of the FBC technology should, therefore, be subject to the same regulations and standards as any coal-fired facility. Any water quality monitoring requirements applicable to conventional coalfired facilities are equally applicable to FBC of coal plants. Based on theoretical and available experimental information, the waste streams from FBC installations and the appropriate pollution control systems will meet applicable discharge standards, including those directed toward disposal of solid wastes in landfills or by other means.

The FBC water quality monitoring strategies proposed in this section primarily address regulated pollutants. However, other pollutants are included in the proposed monitoring programs either because of proposed regulations or because such pollutants are present or could potentially be present in the FBC waste streams. Some of the other pollutants are included in the monitoring programs because of their potential as indicators of pollution, or because of their hazard potential.

This section covers the water quality impact generators, conditions under which ambient (or other type of monitoring) is required, the applicable regulations, selection of pollutants to be monitored, design of the monitoring systems, applicable water quality measurement and data analysis methodologies.

IMPACT GENERATORS

Several potential impact generators were identified in Section 2. Proper engineering should prevent degradation of the groundwater at the plant site and at the site of disposal of solids. Proper design and operation of wastewater treatment facilities at the plant site should also prevent contamination of any surface waters potentially impacted by the plant.

Three impact generators may have a potentially significant impact upon groundwater quality during operation of an FBC facility:

- Leachate from coal and sorbent storage piles
- Infiltration from cooling water ponds or canals, if used
- Leachate from disposal of solid wastes

Impact generators which may affect surface water quality include:

- Chemicals used for treatment of water used in boiler and cooling tower operations
- Leachate from coal and sorbent storage piles
- Aqueous wastes from regeneration operations
- Potential aqueous waste resulting if on-site hydration is used to treat solid wastes prior to landfill disposal

The aqueous effluents generated by use of FBC technology and accessory power-generating equipment would probably be regulated under the National Pollutant Discharge Elimination System (NPDES). Under this system, the state in which a facility is located would determine: 1) limits of pollutant concentrations in the effluents, and 2) effluent monitoring requirements based on effluent standards for steam electric power-generating facilities; the use, classification, and water quality of the receiving surface water; and additional information on specific processes which generate regulated pollutants and/or pollutants which may be hazardous.

CONDITIONS WHERE AMBIENT WATER QUALITY MONITORING IS INDICATED

The variations in processes which could be used and types of pollutants generated as a result of the processes have been summarized in Section 2. The complexity of operations at a facility employing FBC as an energy conversion process will determine the need for or requirements of an ambient water quality monitoring program.

A potential source of water pollutants common to all coal combustion facilities results from storage of the coal, and, in the case of FBC, from the storage and handling of the sorbent and the solid wastes from the combustion process. If coal, sorbent, and the generated solid wastes are stored in areas exposed to the weather, leachate formation, and subsequent contamination of surface and groundwaters may occur. The coal leachate may contain contaminants which are potentially mutagenic. Therefore, a facility which stores solid materials in a manner which allows formation of leachate and subsequent contamination of water resources would be a candidate for source-oriented ambient monitoring. If the solid materials are not exposed to weather, as at the Georgetown University FBC facility, the potential for generation of contaminants and for contamination of the water resources would be minimal and ambient monitoring of the water resources would not be indicated.

The processes summarized in Section 2 list several direct aqueous effluents, each of which may contain numerous pollutants. If a facility employing the FBC technology does not utilize boilers or other processes which would generate aqueous effluents, an ambient monitoring program would not be indicated. If processes or equipment such as boilers, cooling towers, or ponds are employed, effluents from the facility would be regulated in the same manner as conventional coal-fired facilities.

Other processes that could be employed at an FBC facility, e.g., sorbent regeneration and hydration of solid residues prior to transportation to a disposal site, would indicate a need for an ambient monitoring program. If either of these two processes are employed, aqueous effluents specific to the FBC process will be generated. If the generated wastes are discharged untreated to a water resource, an ambient monitoring program would be indicated. If, however, the wastewater is either treated on-site and discharged to a sanitary sewer or discharged directly to a sanitary sewer, an ambient monitoring program would not be necessary.

Disposal of the solid wastes generated by the FBC technology would, in general, require an ambient monitoring program at the site of disposal or in the water resources which

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may become contaminated by leachate or direct spillage of the solid wastes. An exception would occur if the solid wastes were used to produce "concrete" blocks or were used as roadbed fill. In this event, their suitability for the intended use would have to be determined, as would the amounts and types of pollutants generated and their fate as a result of such use. An ambient monitoring program, however, would not be required at that time.

In summary, the conditions under which an ambient monitoring program would be indicated are restricted to the disposal of solid wastes and aqueous effluents or pollutants unique to FBC technology. Monitoring of aqueous effluents is further restricted to cases where the effluents are discharged directly to a receiving water or storm sewer rather than to a sanitary sewer. The aqueous effluents unique to FBC technology include those resulting from the regeneration process and possibly from hydration of the FBC solid wastes.

The aqueous effluents and water pollutants resulting from operation of an FBC unit include two generic sources. Those resulting from coal pile drainage and use of power generating equipment are similar to those produced by conventional coal-fired power plants, with the exception of drainage from piles of sorbent and accessory spent bed material handling or regeneration operations. The second primary source of water pollutants is from disposal of the solid wastes, bed reject material and fly ash which has been collected by precipitators, baghouses, or cyclones.

Solid wastes are either buried in a landfill or are reused in some form. Three main areas for use of the solid wastes can be identified:

- Agricultural
- Commercial/Industrial
- Environmental (Land Reclamation)

The primary uses of solid wastes for agricultural purposes are for application of the spent bed material to acid soils to increase their fertility or for soil conditioners. For some crops, the materials may be employed as a direct source of soil nutrients.

The commercial/industrial uses of the solid wastes may include the spent bed material and the collected fly ash. The uses may include:

- "Concrete" blocks for building construction

- Aggregate for road-base construction
- Use as gypsum products or raw material for such construction
- Recovery of metals
- Use for construction of artificial reefs

In land reclamation, the high pH and alkalinity potential of the solid wastes may ameliorate or neutralize the effects of "acid mine leachate," which occurs in conjunction with both strip mining and deep mining of coal. The use of the material to neutralize the effects of acid rain upon areas such as the Adirondacks would also be considered as constructive landfilling/land farming/land reclamation.

Monitoring to determine the effects of the FBC solid wastes and the individual pollutants on the environment from the utilization of solid wastes for any of the cited uses will not be included in this report. The EPA should, however, continue its programs to determine the environmental effects of emissions or effluents from solid waste utilization processes (Henschel, 1979).

The following discussion will concentrate on the possible effects and consequent ambient monitoring requirements necessitated by the direct aqueous effluents of the FBC technology and its accessory power generation or conversion processes, and the indirect aqueous effluents resulting from landfill disposal of FBC solid wastes.

Although nearly all EPA regulations may apply to some portion of the aqueous effluents generated by operation of an FBC unit, two sets of regulations are likely to predominate. Direct aqueous effluents discharged to surface or subsurface waters would be covered by the NPDES regulations. Disposal of solid wastes generated by FBC would be covered by the Resource Conservation and Recovery Act (RCRA) regulations.

In 40 CFR, Part 261 of RCRA, the four categories under which a waste material may be classified as hazardous are: 1) toxicity, 2) ignitability, 3) corrosivity, and 4) reactivity. Toxicity of a waste is based on the concentration of eight trace metals present in the leachate of the waste when the leachate is generated by a specified procedure, using a dilute acetic acid solution as the solvent. If the concentrations of any of the eight trace elements in the leachate are greater than one hundred times the allowable concentrations stated in the National Interim Primary Drinking Water Regulations (NIPDWR), the waste may be considered toxic and therefore hazardous. In a recent test of several solid residues from both Atmospheric and Pressurized FBC units, none of the residues were found hazardous according to the leachate toxicity test (Sun and McAdams, 1979).

The remaining three classes of hazardous materials are not likely to apply to FBC solid wastes. The solid wastes are not expected to contain sufficient unburned carbon to be ignitable, nor would they be expected to cause fires through friction, spontaneous chemical changes, or retained heat. This assumes, however, that the solid wastes, particularly the spent bed material, have been allowed to cool to ambient temperature prior to introduction into a landfill site. If the wastes are landfilled while still hot (in excess of 250°C), the potential exists for causing fires if combustible wastes such as cloth, paper, wood, or other organics are also present in the landfill.

Corrosivity may apply to FBC wastes. If the spent bed material is hydrated prior to shipment to a landfill for disposal, the resultant slurry can be defined as corrosive, since the pH of the slurry would be greater than 12.

The residual calcium oxide content in the FBC solid wastes, particularly the spent bed material, could cause the release of appreciable quantities of heat upon hydration. However, the amount and nature of the heat released is not believed to be sufficient to cause the wastes to be classified as reactive (Henschel, 1979).

In addition to the pollutants listed in Table 41, the EPA has announced water quality criteria for 27 of the 65 criteria pollutants (EPA, 1979d). Of the 27 pollutants, 8 may be significant in assessing potential impacts of FBC effluents on the environment. Seven are metals, and one an organic compound, fluoranthene, which has been detected in Level 1 or Level 2 analysis of FBC effluent streams. Some of the elements have significantly different values than those listed in the National Interim Primary Drinking Water Regulations. For example, the criterion listed for silver is 10 μg/ℓ for protection of health, and 0.0090 μg/ℓ for protection of freshwater aquatic life. Beryllium and thallium are included in the criteria, and values are provided for protection of human health. The lead, beryllium and cadmium criteria for freshwater are based on the hardness of the water. The suggested criteria for fluoranthene are 200 μg/ℓ for protection of human health, 250 μg/ℓ for protection of freshwater aquatic life, and 0.30 μg/ℓ for protection of marine organisms.

These criteria were developed in accordance with Section 304(a) of the Clean Water Act and are not water quality standards. The criteria would become standards only if adopted by

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TABLE 41. APPLICABLE AMBIENT WATER QUALITY STANDARDS[a]

Pollutant	NIPDWR[b]	NSDWR[c]	Irrigation[d]
Aluminum			5.0
Arsenic	0.05		1.0(0.1)[e]
Barium	1.0		
Beryllium			0.1
Boron			0.75
Cadmium	0.01		0.01
Chloride		250	
Chromium	0.05		0.10
Cobalt			0.05
Copper		1.0	0.20
Fluoride	2.4[f]		1.0
Iron		0.3	5.0
Lead	0.05		5.0
Lithium			2.5
Manganese		0.05	0.2
Mercury	0.002		
Molybdenum			0.01
Nickel			0.2
Nitrate-N	10.0		
Selenium	0.01		0.02
Silver	0.05		
Sulfate		250	
Total Dissolved Solids		500	5000
Zinc		5.0	2.0
pH		6.5-8.5	4.5-9.0

[a] All concentrations in mg/ℓ except pH.

[b] EPA, 1978c.

[c] EPA, 1977a.

[d] National Academy of Engineering, 1973.

[e] EPA, 1976c.

[f] Limit based on mean air temperature for the region of use.

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a state or the EPA under Section 303 of the Clean Water Act. The criteria are useful in assessing the importance of pollutants.

Sections 265.90-94 (Subpart F) of RCRA also describe the testing and analysis required to determine the background levels of the quality of groundwater underlying the facility. In general, the parameters to be monitored during the various phases of the program include:

- Specific conductivity
- Chloride
- Total dissolved solids
- Dissolved organic carbon
- Principal hazardous constituents or indicators thereof found in the largest quantity in the hazardous waste
- National Interim Primary Drinking Water Regulation parameters
- National Interim Secondary Drinking Water Regulation parameters
- Beryllium
- Nickel
- Cyanide
- Phenols
- Organics (scanning by gas chromatography)

Some pollutants listed are not expected to be contaminants in the solid wastes from FBC units. These parameters include phenols, organics, pesticides, radioactivity, cyanides and organic carbon. While these pollutants are not expected to be a problem with FBC solid wastes, their background concentrations should be determined in the groundwater. Determination of background concentrations and continued monitoring for these pollutants would be desirable because of the possible range of types of solid wastes which may be disposed of in a landfill with the FBC wastes. Mixtures of different wastes could result in alteration of leachate composition with respect to that generated by either of the wastes, with potential significant adverse affects upon the environment.

SELECTION OF POLLUTANTS TO BE MONITORED

Selection of pollutants which should be monitored will use information generated in Level 1 and Level 2 analysis of FBC unit effluents, and other applicable tests. Applicable existing and proposed effluent and ambient standards are used to provide an initial basis for segregating the potential pollutants among three categories. The applicable regulations and sources of desirable pollutant limitations include:

- National Interim Primary and Secondary Drinking Water Regulations
- Resource Conservation and Recovery Act, Section 265,Subpart F
- EPA Quality Criteria for Water
- EPA Consent Decree for Criteria Pollutants
- Recommended Limits of Pollutants in Water Used for Continuous Irrigation
- Electric Power Plant Effluent Guidelines

Determination of toxicity or hazard potential of the pollutants was made by use of Minimum Acute Toxicity Effluent values, and by the carcinogenicity ratings of compounds listed by the National Academy of Science (1972). The procedure for selection of pollutants described in Section 3 was employed.

Minimum Acute Toxicity Effluent (MATE) values have been developed for most of the elements (Cleland and Kingsbury, 1977). MATEs describe maximum desirable pollutant concentration in effluents, and have been developed for most elements as well as numerous organic species. Comparison of the concentration of species in an effluent, in this case the leachate from FBC solid wastes, with the respective MATE values provides an estimation of which of the elements may pose a threat to public health or ecological stability. For the water media as well as for the air and land media, MATE values are available for both health and ecology. Where they differ, the most restrictive value was chosen for comparison with the leachate data. The significance of a given element is determined by the ratio of concentration to the MATE value. Three levels of significance have been identified: the first level includes those elements whose ratios are greater than 1; the second, elements with ratios ranging from 0.1 to 1; and the third, elements having ratios less than 0.1.

Elements whose concentrations in the leachate of the FBC solid wastes exceed the most restrictive MATE values include:

Lithium
Boron
Magnesium
Aluminum
Silicon
Phosphorus
Selenium
Sodium
Iron
Zinc
Manganese
Potassium
Calcium
Lead
Titanium
Vanadium
Nickel
Copper
Chromium
Arsenic
Silver

Elements whose ratio of concentration to MATE values were between 0.1 and 1 include:

Barium
Beryllium

Elements whose ratios of concentration to MATE values were less than 0.1 include the following, plus all other elements not included in Tables 19 or 20:

Fluorine
Chlorine
Scandium

Cobalt
Gallium
Rubidium
Strontium

Yttrium
Zirconium
Molybdenum

Lanthanum
Cerium
Niobium
Tungsten

Tin
Antimony
Thallium[a]

Rhodium[a]
Mercury[a]
Cadmium[a]

Sulfur, although high in concentration, was not compared to the MATE values, since it was predominantly present in the form of sulfate, particularly calcium, magnesium, sodium or potassium sulfates. The sulfates of the metals are included in determination of respective MATE values.

Some forms of polycyclic organic matter (POM) were measured on the solid wastes in three studies (Merryman et al., 1977; Pillai and Roberts, 1977; Ryan et al., 1979). The data obtained in the former two studies are summarized in Table 11. To assess the impact of solid waste upon the water media, it is necessary that the contaminants in the solid waste become dissolved in water or at least be in suspension and available for absorption or ingestion by organisms. If we assume that all of the contaminants measured will be dissolved in a single aliquot of water, and the volume of water is equivalent to the weight of the solid waste, none of the POMs would exceed the MATE values for water. Only two of the POMs, benzo(a) pyrene, and dibenzo(a,h) anthracene, would have a concentration to MATE value ratio greater than 0.1.

Major anionic species such as nitrate, nitrite, sulfate and sulfites are not included in the list MATE values separate from a cation, although the anions may have toxic properties of their own separate from any cation. Pertinent anion data from some leachate studies on FBC solid wastes are summarized in Table 21.

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[a] These metals have low MATE values or are highly toxic; however, their concentrations were consistently below the detectable limit of the analytical method employed.

Two distinct process effluents can affect the quality of water; therefore, each effluent type will be processed separately: 1) solid wastes, including bed reject material and collected flue gas particulates, and 2) the liquid waste streams associated with power generation and those associated with sorbent regeneration and on-site hydration of the solid wastes. Based on the National Interim Primary Drinking Water Regulations, the pollutants belonging to Category I include:

Arsenic
Barium
Cadmium
Fluoride
Chromium IV
Lead
Mercury
Nitrate-N
Selenium
Silver

The standards for the pesticides, radioactivity, and bacteria do not apply to FBC solid wastes, and therefore are not included in Category I.

Development of the Category II pollutants list uses the proposed Secondary Drinking Water Regulations, the Resource Conservation and Recovery Act Section 265, and the 27 pollutants listed in the EPA Consent Decree for Criteria Pollutions, for which ambient standards have been proposed. Once again, pollutants not applicable to FBC solid wastes are not included in the list. The pollutants in Category II include:

Chloride
Copper
Iron
Manganese
Sulfate
Nickel
Organics
Total Dissolved Solids
Zinc
Thallium
Fluoranthene
Beryllium
Dissolved Organic Carbon
Specific Conductivity

Pollutants included in a list used to develop Category II pollutants already included in Category I were not duplicated.

The Level 1/Level 2 analysis of leachate of FBC solid wastes indicates that 11 additional elements are present in concentrations which exceed MATE values but are not regulated at the federal level as a drinking water or ambient standard. These include:

Lithium
Boron
Magnesium
Aluminum
Silicon
Phosphorus
Sodium
Potassium
Calcium
Titanium
Vanadium

All of these elements are candidates for inclusion in an ambient monitoring program. They are present in high concentrations and therefore may indicate pollution of the ground water. Major elements on this list, such as calcium, magnesium, sodium, potassium, or silicon, could be used as indicator or support parameters, while the remainder would not be considered as pollutants for monitoring. If a hydrologic survey indicates that an aquifer being used as a source of irrigation water has the potential to be contaminated by FBC solid waste leachate from a landfill or other source, additional pollutants could be added to Category II. The pollutants which could be added include boron, aluminum, cobalt and lithium.

Those pollutants not included as candidates for monitoring could be included if the hazard potential for the pollutants so indicate. Determining the actual hazard potential of these pollutants requires information such as the amount of leachate formed, the concentration of pollutants in the leachate, the dilution ratio of the leachate by the groundwater into which the leachate discharges, and the rate of attenuation of the pollutants by soil and other geologic formations.

The pollutants in Categories I and II could be increased in numbers if state regulations for maximum concentration of pollutants are included in the decision model. If state regulations are not considered, Category III pollutants will include all of those not included in Categories I and II. The pollutants included in the three categories are summarized in Table 42.

TABLE 42. SUMMARY OF POLLUTANTS SEGREGATED AMONG CATEGORIES

Category I	Category II	Category III	
Arsenic, Barium	Chloride, Copper	Titanium	Gallium
Cadmium	Iron, Manganese	Vanadium	Uranium
Fluoride	Sulfate, Nickel	Boron	Thorium
Chromium IV	Zinc, Thallium	Silicon	Cobalt
Lead	Beryllium, Fluoranthene	Sodium	Palladium
Mercury	Total Dissolved Solids	Potassium	Platinum
Nitrate-N	Dissolved Organic Carbon	Nitrite	Lanthanides
Selenium	Specific Conductivity	Sulfite	Actinides
Silver	Organics (specific and general)	Rubidium	
Calcium	Benzo(a)pyrene		
Magnesium	Benzo(a,h)anthrance		
	Lithium		
	Aluminum		
	Phosphorus		
	Sulfide		

The pollutants discharged in aqueous effluents at an FBC site will depend on the processes used; the type and number of pollutants included in each category also depend on the processes used, including those used to treat the wastewater. Table 43 lists those pollutants regulated in effluents in power plants using chemicals for water treatment. The pollutants produced by the FBC process may include any of those listed in Tables 11, 18, and 19. Since the effluent streams containing these pollutants would be treated along with other effluent streams generated at a site, the potential number of pollutants discharged is very high. The number could increase if chlorinated effluents from cooling tower blowdown are treated along with coal pile drainage or liquid effluents from hydration of solid wastes. Many of the organic compounds would, however, be absorbed into the suspended solids, most of which would be removed during the wastewater treatment process.

While most of the pollutants would in all likelihood be removed from the wastewater prior to discharge, if a sufficient number and quantity were discharged, the result would be a low-level, long-term impact upon the aquatic ecosystem. The solid waste pollutants categorized in Table 42 are also to be included in monitoring for aqueous effluents which may be discharged directly to a surface water or infiltrate from sedimentation basins into the groundwater. However, because of the higher potential for organic pollutants to be discharged at the plant site, more specific organics would be included in the monitoring requirements.

The organic pollutants which should be included in the three categories for ambient water quality monitoring programs are: Category I, Category II (fluoranthene, benzo(a)pyrene, and dibenzo(a,h)anthracene), and Category III (all other organics listed in Table 11).

The pollutants listed in Table 43 would be included in Category I for sampling and analysis of plant effluents, but would be included in Category II for monitoring programs aimed at determining water quality of the receiving waters. In case of duplication, of course, pollutants would remain in the lowest numbered category consistent with applicable standards.

The four areas of ambient water quality monitoring required for FBC facilities are listed below and discussed in the following sections:

- Groundwater
- Surface Water
- Physical Sinks
- Biological Sinks

43

TABLE 43. SELECTED EPA EFFLUENT STANDARDS FOR STEAM ELECTRIC POWER GENERATING PLANTS (Greenwood et al., 1979)

Pollutant or characteristic	Maximum one day[a]	Average of daily values for 30 consecutive days shall not exceed[a]
pH (all discharges)	6.0 - 9.0	
Polychlorinated Biphenyl Compounds	No discharge	
TSS	100.0	30.0
Oil and Grease	20.0	15.0
Total Copper from Metal Cleaning or Boiler Blowdown	1.0	1.0
Total Iron from Metal Cleaning or Boiler Blowdown	1.0	1.0
Free Available Chlorine from Cooling Tower Blowdown	0.5	0.2
Materials Added for Corrosion Inhibition in Cooling Tower Blowdown	No detectable amount	
From Cooling Tower Blowdown		
Zinc	1.0	1.0
Chromium	0.2	0.2
Phosphorus	5.0	5.0
Heat from Main Condensers	None	

[a] Expressed in mg/ℓ except pH.

GROUNDWATER MONITORING

The groundwater monitoring which would be required as a result of operation of FBC facilities includes areas around landfill sites where FBC wastes are disposed of, and areas or aquifers around the FBC facility if that facility has the potential to contaminate the groundwater from coal sorbent waste solids, pile leachate, canals, or ponds used for cooling water or for sedimentation.

An additional source of potential contaminants is flue gas particulates which settle on the ground around the facility. Little is known about the amount of flue gas particulates which may settle on the ground, the area which may be affected, or the potential for groundwater contamination. Most probably the filtering and absorption capacity of soil would prevent groundwater contamination from this source.

The methods to be employed in selection of groundwater sampling locations, the methods of sampling and the costs involved, have been adequately summarized (Todd et al., 1976; Everett et al., 1976). When applying the methods detailed in summaries, the specific requirements of the states which have been implemented in groundwater monitoring or quality programs must be adhered to, if a facility is located in a state with such a program. The groundwater monitoring program must also accommodate the monitoring requirements proposed in the Resource Conservation and Recovery Act, Section 265, Subpart F. The RCRA monitoring requirements are addressed to monitor the source for any pollutants so that appropriate actions can be taken to prevent groundwater contamination if the leachate quality demonstrates the need for such actions. The required RCRA monitoring system can be a functional part of the source-oriented groundwater monitoring system and can be used as an early warning system for potential problems.

SURFACE WATER MONITORING

The surface water monitoring which would be required as a result of operation of FBC facilities includes the surface waters receiving direct discharges from a facility, and those receiving indirect discharges from airborne particulates or from contaminated groundwater which discharges to a surface water. The surface water for which an ambient monitoring program must be designed includes rivers and streams, lakes and ponds, estuaries, and oceans.

Each surface water resource may require a slightly different strategy to effectively monitor water quality and changes in water quality induced by operation of an FBC facility.

PHYSICAL SINKS

Physical sinks are caused primarily by precipitation, sedimentation or absorption of pollutants into or onto the bottom sediments of a body of water. The characteristics which cause these actions include solubility, density, and partition coefficients. Physical sinks are not permanent, and materials contained in the sinks may be recirculated through the water column or biotic component of the ecosystem if conditions change. An example of recirculation is the mercury contamination of Lake St. Clair. Mercury metal discharged to the lake was, in theory, to remain permanently in the sediments and remain harmless to the environment. However, long-term action by bacteria produced methylmercury which is soluble and assimilatable; it consequently bioaccumulated in high concentrations in fish, rendering them unfit for consumption. Similarly, a physical-chemical process may move contaminants out of a sink. When a lake such as Lake Erie becomes anoxic, a reducing environment is initiated and pollutants such as iron and phosphorus can be solubilized and "move" from the sediments to the water layer.

A third mechanism of pollutant removal from physical sinks is direct ingestion of the pollutant by animals. The animals may be oligochaetes who are subsequently consum[illegible] by higher forms, or fish such as carp, sturgeon or catfish. In any event, pollutants deposited in physical sinks may not remain there permanently.

Physical sinks may occur in all types of surface waters; however, their importance varies with the type of surface water. A shallow stream with a moderate to swift current, while not amenable to formation of physical sinks, often has pools formed at bends or wide parts where a sink can form. In general, all surface waters where the current is drastically reduced, including lakes, ponds and oceans, may have physical sinks that can be sampled.

The conditions under which a physical sink should be included in the source-oriented ambient monitoring are:

- All surface waters where an FBC facility is the primary discharge to the system either from direct aqueous effluents or indirect effluents from landfill leachate.

- Surface waters where the type of pollutants discharged by an FBC facility differ significantly in speciation from other discharges to that surface water.

- Times when biological surveys indicate that the biota of the receiving water is changing in diversity or quality.

- After any spills of FBC process wastes reach the surface water due to either direct discharge or discharge via leachate.

BIOLOGICAL SINKS

Biologic uptake of a pollutant represents another sink. Bioaccumulation of a toxic compound can have extremely adverse consequences for an organism, ranging from ill health, to failure to reproduce, to death. There are two mechanisms for uptake, ingestion and absorption through the surface membranes. Internally, a number of processes occur: the material may be stored; the material may be excreted; or the material may be chemically altered, producing a product which again may be stored, excreted, or further altered. Occasionally, the secondary reaction products are more toxic than the compound initially taken in.

Even if a pollutant is present in the ambient environment in concentrations below the minimal detection limits, bioaccumulation can magnify its concentration by factors of 10^3 or 10^4. For example, the ecological magnification of chlorobenzene in a model aquatic ecosystem was 650. In another study, the factor for tetrachlorobiphenyl was 17,840 (Branson, 1978). Polynuclear aromatic hydrocarbons, because of their high partition coefficients, are expected to bioaccumulate.

The next problem is assessing the hazard to an organism as a result of compound accumulation. An additional variable is introduced by unpredictable synergistic and antagonistic interactions of pollutants.

Monitoring of the biological components of the aquatic environment in a source-oriented ambient program is indicated when:

- A process analysis of the FBC facility indicates the potential for release of compounds known to be toxic or to bioaccumulate.

- Species in the receiving water are known to be unusually sensitive to an effluent from the facility.

- The type of pollutants discharged by an FBC facility differ significantly in speciation from other discharges to that water.

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- Biological monitoring is the best method to determine the lowest detectable concentrations allowable.
- Surveys indicate that the biota of the receiving water is changing in diversity or quality.
- Pollutant containment systems fail, resulting in a catastrophic discharge to a receiving body of water followed by reestablishment of the biological community.

In lieu of a specific need, synoptic surveillance is all that would be required for a monitoring program. In such a program, the presence and abundances of the major populations in the ecosystem are determined on an overview basis. If needed, target monitoring must be done: this might include necropsy, histopathology and chemical analysis.

CONSIDERATIONS SPECIFIC TO SURFACE WATER MONITORING

Because different areas possess different hydrological conditions, a good monitoring program must take into account local variations. To do this, the hydrological characteristics of the area or basin to be monitored must be determined. In this and the following section on groundwater monitoring, general strategies for hydrological and geological characterizations as they relate to developing a good, comprehensive water quality monitoring program will be discussed.

Definition of the Watershed and the Hydrological System

The term "watershed" refers to a given geographical area in which all the water flows to or through one point. It includes both the land and the bodies of water in the area. Watersheds vary widely in their size and configuration, and a number of small watersheds may comprise a larger one if all water flows to a common point. To define a given watershed, the common point of flow is identified and then, "working upstream" on a topographic map, all contiguous areas from which water will run off or flow downhill to that common point are determined. The watershed is not equatable with the hydrologic system. The latter also includes groundwater, which may have a net inflow or outflow relationship with the surface waters. Their geographical limits are seldom identical.

The goal of characterizing the hydrologic system is to determine where the water is, how much there is, and where and how it is moving through the system. In order to determine this, the following information is needed:

- Precipitation--the amount, duration and intensity of rain and snowfall. Seasonal distribution is important.

- Surface Waters--number, location, size, source and destination. This information indicates where the water is going in order to help identify possible pollutant sinks.

- Evaporation and Transpiration Levels--based on the climate, area of open water, topography, volume, and type and distribution of plant cover. Transpiration may be the most important component of total evaporation. Vegetation surveys are required to determine this parameter.

- Run-off--direction, magnitude, and destination of run-off. This is a major contribution to stream flow and major cause of erosion. This is especially important during the construction phase of a project.

- Infiltration--rate at which surface waters enter the groundwater system. This is a function of local soils and bedrock geology.

It is also important to ascertain all the administrative jurisdictions in the watershed to identify which environmental regulations may apply and who may already be monitoring water quality within the watershed.

Transport of Pollutants in Surface Aquatic Systems

The ability of pollutants to be transported through the surface aquatic systems is of great importance, especially when evaluating the effects of a technology on the biological components of the surface areas. Factors of importance are:

- How fast will the pollutant travel through the system? (What is the velocity of the hydrological components receiving the pollutant?)

- Where (and how far) will the pollutant be carried?

- How concentrated will the pollutant be at some point downstream. (What is the dilution factor/capacity of the hydrological systems?)

- What is the final receiving system for the pollutant? Is it a particularly sensitive system?

- How will the pollutant disperse? This is especially important in standing bodies of water which may not have an obvious direction of current flow.

- How will the pollutant be chemically transformed in the environment?

These factors evaluate the mobility of pollutants in a hydrologic system and help to evaluate the impact of an FBC facility on an area. A pollutant may move through the system in question so rapidly that there will be no impact on that system. This does not mean that a system downstream will not be affected. The possible impacts on surrounding systems may also have to be assessed.

CONSIDERATIONS SPECIFIC TO GROUNDWATER MONITORING

The following sections present a general strategy or approach for designing a groundwater monitoring program. Since geologic and hydrogeologic conditions vary from site to site, the strategy must be flexible to allow for local conditions while at the same time providing a logical and consistent design approach which can be applied to any and all potential sites. Although many different types of monitoring have been identified by the EPA (i.e., source, case preparation, research, and ambient trend monitoring), the focus here is on ambient trend monitoring, which characterizes existing conditions and temporal and spatial trends in groundwater quality relative to federal, state, and local standards (Todd et al., 1976).

The following is a step-by-step approach to be used in developing a groundwater quality monitoring program: (1) define the area or basin to be monitored, (2) define the physical/geological system of the basin, (3) define the hydrogeologic system of the basin, (4) evaluate the ability of wastes to infiltrate at the land surface, (5) evaluate the ability of pollutants to percolate from the land surface to the zone of saturation, and (6) evaluate the attenuation of pollutants in the saturated zone (Todd et al., 1976). These steps are discussed in more detail below.

The first step is to define the area or basin in terms of hydrogeological and administrative and political frameworks. Groundwater basins may, but usually do not, have the same drainage boundaries as the overlying surface water system. Federal, state, and local agencies can assist in defining the basin. The exact lateral and vertical extent of the basin cannot be identified with certainty until the second and third steps have been completed. Administrative and political frameworks should be identified early in the project to determine (1) who may be monitoring groundwater in the

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(PREVIOUSLY EIN. EPA FORM 287)
TYPING GUIDE SHEET

basin, (2) what agency(ies) has (have) jurisdiction over the basin, and (3) what permits or other legal requirements may be necessary to implement the program. Early identification of these items will prevent duplication of efforts and unnecessary expenditure of funds.

The second step is to define the physical system of the basin which consists of the soils, vegetation, and unconsolidated and bedrock deposits found on and underlying the basin. These materials should be inventoried as to number and spatial distribution. Particular emphasis should be placed on the physical properties such as permeability, porosity, and thickness which affect the ability of the materials to transmit groundwater. Mineralogy and chemical characteristics of the materials should be identified in order to determine potential effects on water quality. For example, clay minerals have the ability to remove ions from solution while other minerals, e.g., sulfides, may go into solution to be deposited later as sulfates.

Information on the physical system can be obtained from federal and state EPA's and geological surveys, soil surveys, and from universities. In the event that data are not already available, it becomes necessary to generate data using field techniques. Exploratory drill holes and soil samples and seismic and earth resistivity surveys will usually provide the information necessary to characterize the system. Spacing between drill holes, soil samples, and seismic and earth resistivity surveys will vary with the geologic complexity of the site.

The goal of this third step is to determine where the water is going, how much of it is going, how it is going, and when it is going. In order to achieve this goal the following hydrogeologic data are required (Todd et al., 1976):

- Aquifer characteristics--locations, depths, extent, transmissivities/transmissibilities (source: geologic and pump test data)
- Groundwater levels--elevations of water in wells (source: well observations)
- Depths to groundwater--interpretation of groundwater level and topographic data (sources: well observations and topographic data)
- Locations and magnitudes of groundwater recharge areas--areas where surface water infiltration contributes to the groundwater system (source: precipitation, evapotranspiration, soils, land use, and water level data)

- Locations and magnitudes of groundwater discharge areas--areas where groundwater contributes to the surface water system (source: stream flow data, water level data, and aerial photographs)

- Directions and velocities of groundwater flows--characterization of flow system (source: water level and transmissivity data).

Groundwater flow system diagrams will indicate directions of flow at various depths and the piezometric surface of the groundwater. Once the flow system(s) has(have) been defined, the geometry of pollution plumes migraling in the zone of saturation and the potential for pollution of other water resources can be identified. Mapping of the flow system identifies groundwater recharge and discharge zones and whether the flow enters the local or regional flow systems. The relationship of pollutant sources to recharge and discharge zones will indicate the potential for pollution of other water resources. For example, the release of pollutants in a discharge zone will pollute surface waters but will not affect groundwaters.

Evaluation of Ability of Pollutants to Percolate From the Land Surface to the Zone of Saturation

The ability of pollutants to leach from coal piles, landfills, and holding ponds is the chief factor creating the need for a groundwater monitoring program. If the wastes cannot infiltrate the land surface, they cannot pollute the groundwater system.

The quantity of leachate from coal piles and landfills can be computed using the water balance method. The quantity of leachate (Q_P) is equal to the precipitation (P) minus runoff (R), evapotranspiration (ET), and the field capacity of the material, excluding the existing moisture content (S):

$$Q_P = P-R-ET-S \tag{24}$$

The quantity of leachate leaving a coal pile or landfill is determined by the ability of the underlying soils, unconsolidated deposits, and bedrock to transmit water. The quantity of leachate can be determined by comparing the quantity of leachate produced (Q_P) and the maximum quantity of infiltration (Q_I), determined as the product of the materials permeability (K) and the area of the pollutant source (A), if Q_P exceeds Q_I. However, if Q_I exceeds Q_P, then the quantity of leachate leaving the source (Q_L) equals Q_P. The ultimate quantity of leachate reaching the zone of saturation is determined by the storage capacity requirements of the material between the water table and the surface, the attenuation ability of the earth materials, and the leachate control method employed on-site.

Evaluation of Attenuation of Pollutants in the Vadose Zone

As stated, the ultimate quantity of pollutants reaching the zone of saturation is partially a function of the storage capacity requirements of the materials between the water table and the surface. In arid and semi-arid lands, pollutants may be taken up into storage and effectively prevented from reaching the groundwater table. However, the vadose zone, the area between the zone of saturation and the surface, does not always remove pollutants. At times, the vadose zone is bypassed by the discharge; in humid environments, infiltration is a virtually continuous process.

A discussion of the ability of pollutants to percolate through the vadose zone and reach the groundwater system must focus on the ability of the materials in the vadose zone to attenuate pollution. Pollution may be attenuated by the following processes; however, the attenuation must be evaluated for each process for each pollutant. The attenuation processes are (1) dilution, (2) filtration, (3) sorption, (4) buffering, (5) chemical precipitation, (6) oxidation and reduction, (7) volatilization, (8) biological degradation and assimilation and (9) radioactive decay (Todd et al., 1976).

Dilution occurs when water from other sources infiltrates the land surface. Dilution in the vadose zone can be significant in humid regions and non-existent in arid and semi-arid regions. Dilution is computed in the same manner as infiltration but all sources of infiltration are considered, e.g., leakage from streams, lakes, and canals, and artificial recharge.

Filtration removes particles with effective diameters larger than the pore spaces of the earth material. Almost all suspended solids are removed by this process. The filtration process eventually prevents the passage of all water as the pore spaces become blocked with solid material. Filtration is essentially ineffective in removing elements and inorganic compounds.

Sorption is the dominant attenuation process in clay-rich earth materials. In sorption, electrically neutral pollutants, such as most organics and some metals, are removed from solution and bound to the clay minerals. However, the sorbed materials may be taken back into solution by migrating groundwater fluids. The ability of earth materials to sorb inorganic substances is finite, but the sorptive capacity for biodegradable substances is renewable.

Buffering, the ability of the soil solution to resist pH change, is directly linked to the sorption of bases; the higher the amount of sorbed bases, the higher the pH. Buffering is usually not important if pH values range from six to nine; however, for other pH values, buffering may affect the ability of the waste solution to carry pollutants.

Chemical precipitation is important relative to calcium, magnesium, bicarbonate, and sulfate, and these ions may precipitate readily in the vadose zone. Other trace elements and compounds which have significant precipitation potential are arsenic, barium, cadmium, copper, fluoride, cyanide, iron, lead, mercury, molybdenum, zinc, and radium.

Oxidation and reduction are important attenuation processes in the top soil layer. Reducing conditions not only cause chemical precipitation but also may cause formation of native elements, including arsenic, copper, mercury, selenium, silver, and lead.

Reactions in aerobic and anaerobic environments may cause volatilization of certain elements and compounds, resulting in their loss to the atmosphere. The elements and compounds which may be affected are mercury, arsenic, selenium, sulfates, and nitrates.

Biological degradation and assimilation are important processes in the removal of organic and biologic materials. Plant uptake effectively prevents pollutants from reaching the zone of saturation; however, unless the plants are disposed of, the pollutants eventually will be recycled to the soil and groundwater systems. The following pollutants are most likely to be affected by this process: sulfate, nitrate, cyanide, mercury, selenium, molybdenum, phosphorus, and potassium.

The final attenuating process affecting pollutant mobility is radioactive decay. Measured as the half-life of the radionuclide, radioactive decay of many radionuclides is a slow process. In most flow systems, its effects are not significant as a means of pollutant attenuation.

Evaluation of Attenuation of Pollutants in the Zone of Saturation

Generally, the same processes of attenuation occur in the zone of saturation as occur in the vadose zone: (1) filtration, (2) sorption, (3) radioactive decay, (4) dilution, (5) oxidation and reduction, (6) buffering, (7) volatilization, and (8) chemical precipitation. Filtration differs only in that movement is horizontal rather than vertical; hence, aquifer area is more important than thickness. There are essentially no differences for sorption, radioactive decay, buffering, and chemical precipitation. Reduction dominates oxidation in the zone of saturation, while oxidation dominates in the vadose zone. Dilution is the primary process of pollutant attenuation in the zone of saturation. The amount of attenuation is determined by (1) the volume of waste reaching the water table, (2) the transmissivity of the aquifer, (3) the vertical and areal hydraulic head distributions, (4) the existing groundwater quality, (5) the quantity and quality of recharge, and (6) the quantity of groundwater withdrawals. Evaluation of pollutant attenuation in the zone of saturation requires considerable judgment by a skilled professional.

SAMPLING

General Considerations

Water quality data can be collected in two basic ways. The first involves collecting water samples which are returned to the laboratory for chemical analysis; the second involves the use of automatic sensor equipment which measures the presence and concentration of particular parameters. Design of a monitoring plan should include an evaluation of the kinds of data collection systems available and their general applicability to the proposed plan. The general physical setting of the facility being studied, parameters to be tested, intensity of sampling and the type of information sought will all be factors in determining what sampling system should be used. In general, a comprehensive monitoring program will probably include elements from both types of systems.

The major elements of any sampling routine include:

- Number of sampling points
- Location of sampling points
- Frequency of sampling
- Volumes collected
- Sample preservation

The importance of each element varies according to the process involved, physical setting of the facility, sensitivity of the receiving waters, goals of the program and the analytical methods used.

Number and Location of Sampling Points--

This factor will be affected by the number of real and potential effluent streams and discharge points associated with the site. The effluent from a holding (settling) pond or treatment plant would usually be sampled as part of a monitoring program. This will be the major water pollution potential of a well-engineered surface facility. However, all

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TYPING GUIDE SHEET

possible effluent streams should be identified. Area runoff may carry "fugitive emissions" and such runoff, if not collected into a holding pond, should be monitored.

Care should be taken to identify all aquifers that may be contaminated during process testing and development, and they should be monitored up-gradient and down-gradient of the test site. For ambient monitoring, one or more sampling locations may be appropriate downstream of the facility with at least one upstream sampling location. If the hydrologic characteristics of the system are adequately known, a dispersion model may be useful for identifying the best sampling locations in terms of likelihood of detecting pollutants.

Representative sampling locations should be selected at sites where the influent, waste, or receiving stream is well mixed. This is at some point below the "mixing zone." The mixing zone may be defined as the point where stream water meets (contacts) water of a different quality, usually effluent wastes (thermal differences are included). The size of mixing zones is controlled by the flow rate of the effluent(s). The EPA guidelines for developing water quality standards state that (EPA, 1976c):

> The total area and/or volume of a receiving stream assigned to mixing zones [should] be limited to that which will: [1] not interfere with biological communities or populations of important species to a degree which is damaging to the ecosystem; [2] not diminish other beneficial uses disproportionately.

The EPA makes no recommendations concerning effluent concentrations within a mixing zone. However, in many states, sampling stations are required within the mixing zone.

It is important that the site be accessible but protected from vandalism, weather extremes, or other damaging factors. The flow of water past the sampling point should be known, either by actual measurement or calculation.

Frequency of Sampling--

The frequency of sampling depends on the flow rate, waste characteristics, and the variability of both. The more uniform the flow and waste composition, the less frequently is sampling required. For a variable flow in which the waste composition is flow-dependent with a known relationship, continuous flow measurement with infrequent checking of pollutant levels may be adequate. However, the usual case involves complicated variability in both flow and composition.

The number of samples taken per unit of time may also reflect the need for statistical analysis of the data. Generally, the more samples taken, the greater confidence accorded to the statistical analyses. This may be limited, however, by the cost constraints placed on the monitoring program. Methods for determining sampling frequency, based on the needs for statistical representativeness of data, cover a variety of conditions ranging from single variable-single to multiple variable-multiple stations (Sanders, 1979). It is, of course, essential that sampling frequency be consistent with the type of data required, the methods by which it will be analyzed and the uses that will be made of the data.

Manual grab samples taken at specified time intervals or following certain waste-generating occurrences are the simplest approach if flows and wastes are uniform or predictable. The approach becomes too manpower-intensive if samples must be taken often (e.g., hourly) or unreliable if inadequate consideration is given to flow or waste variabilities. Automatic sampling is appropriate if flow and waste conditions require frequent sampling. If flow is nearly constant, a non-proportional sampler which obtains the aqueous sample at continuous flow rate is adequate. If the flow is variable, a flow-proportioning sampler at irregular time intervals or a variable volume at regular time intervals is needed. High variability of either flow or composition suggests that an automatic sampler or continuous monitor be installed.

Sample Volumes--

Total volume of samples will be determined by the needs of all the individual waste analyses. The required volume of sample for several water constituents is indicated in Table 44. In general, 1 to 2 liters per sample is necessary at a minimum. Individual portions of a composite sample should be at least 25 to 100 ml.

If more than one laboratory is to analyze the samples for comparative purposes, larger samples should be taken as opposed to taking multiple samples at the same time, because chemical composition may vary between two samples regardless of location and time of sampling.

Sample Preservation--

Perfect or complete preservation of a water sample so as to retain its chemical integrity indefinitely is a practical impossibility. Complete stability of all chemical constituents can never be achieved; for some parameters, their integrity cannot be preserved. Certain chemical and biological processes change the chemical structure and composition of a water sample as soon as it is removed from the parent water source. Preservation is an attempt to retard these chemical and biological processes long enough to return the water sample to the laboratory and perform the appropriate chemical analyses. Methods of preservation are relatively limited, serving to (a) retard biological action, (b) retard hydrolysis of chemical compounds and complexes, and (c) reduce volatility of constituents. Preservation methods are generally limited to pH control, chemical additions, and refrigeration (approx. 4°C); freezing (at 4°C or below) is the best general preservation method. However, it is not applicable to all types of samples and parameters and may not be feasible if the sample site is far from the laboratory. A summary of general preservation methods is given in Table 45.

Sampling Equipment

There are two types of sampling equipment, manual and automatic. The second type can be left in the field for varying periods of time to collect one or several samples. However, these samples must be transported to the lab for analysis.

Manual Samplers--

Most manual water sampling bottles are simply open tubes with movable plugs at both ends. The sampler is lowered into the water to the desired depth and a "messenger" (metal weight) is sent down the cable to activate a release which closes both ends of the bottle. The sample is then brought to the surface, treated as necessary, and stored.

There is a wide variety of sampling bottles used to collect water samples. The choice of one type over another is largely a matter of personal preference. In the absence of a sample bottle, a bucket will suffice for collection of surface water. In general, however, one of the samplers described below is needed when sampling water at depths greater than 3 feet.

The types of manual samplers in common use include Kemmerer, Van Dorn, Nansen, and Fjarlie Samplers. Each sampler operates by slightly different means but will collect similar samples. The principal difference is their adaptability for taking multiple samples. Manual samplers are primarily used when it is necessary to collect only a single sample at a given point in time and space. If a series of samples is desirable at a given point or if a composite sample (over time) is required, the use of automatic samplers would be indicated. A variety of automatic samplers are commercially available which can fulfill the requirements of a

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(PREVIOUSLY CIN. EPA FORM 337)
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TABLE 44. VOLUME OF SAMPLE REQUIRED FOR DETERMINATION OF THE VARIOUS CONSTITUENTS OF INDUSTRIAL WATER
(EPA, 1973)

	Volume of Sample,[a] (ml)
PHYSICAL TESTS[b]	
Color and Odor	100 to 500
Corrosivity	flowing sample
Electrical conductivity	100
pH, electrometric	100
Radioactivity	100 to 1000
Specific gravity	100
Temperature	flowing sample
Toxicity	1000 to 20,000
Turbidity	100 to 1000
CHEMICAL TESTS	
Dissolved Gases:[c]	
Ammonia, NH_3	500
Carbon dioxide, free CO_2	200
Chlorine, free Cl_2	200
Hydrogen, H_2	1000
Hydrogen sulfide, H_2S	500
Oxygen, O_2	500 to 1000
Sulfur dioxide, free SO_2	100
Miscellaneous:	
Acidity and alkalinity	100
Bacteria, iron	500
Bacteria, sulfate-reducing	100
Biochemical oxygen demand	100 to 500
Carbon dioxide, total CO_2 (including CO_3^{--}, HCO_3, and free)	200
Chemical oxygen demand (dichromate)	50 to 100
Chlorine requirement	2000 to 4000
Chlorine, total residual Cl_2 (including OCl^-, HOCl, NH_2Cl, $NHCl_2$, and free)	200
Chloroform-extractable matter	1000
Detergents	100 to 200
Anions:	
Bicarbonate, HCO_3	100 to 200
Bromide, Br^-	100
Carbonate, CO_3^{--}	100 to 200
Chloride, Cl^-	25 to 100
Cyanide, Cn^-	25 to 100
Fluoride, Fl^-	200
Hydroxide, OH^-	50 to 100
Iodide, I^-	100
Nitrate, NO_3^-	10 to 100
Nitrite, NO_2	50 to 100
Phosphate, ortho, PO_4^{---}, HPO_4^{--}, $H_2PO_4^-$	50 to 100
Sulfate, SO_4^{--}, HSO_4^-	100 to 1000
Sulfide, S^{--}, HS^-	100 to 500
Sulfite, SO_3^{--}, HSO_3^-	50 to 100
Miscellaneous:	
Hardness	50 to 100
Hydrazine	50 to 100
Microorganisms	100 to 200
Volatile and filming amines	500 to 1000
Oily matter	3000 to 5000
Organic nitrogen	500 to 1000
Phenolic compounds	800 to 4000
pH, colorimetric	10 to 20
Polyphosphates	100 to 200
Silica	50 to 1000
Solids, dissolved	100 to 20,000
Solids, suspended	50 to 1000
Tannin and lignin	100 to 200
Cations:	
Aluminum, Al+++	100 to 1000
Ammonium, NH_4[c]	500
Antimony, Sb+++ to Sb+++++	100 to 1000
Arsenic, As+++ to As+++++	100 to 1000
Barium, Ba++	100 to 1000
Cadmium, Cd++	100 to 1000
Calcium, Ca++	100 to 1000
Chromium, Cr+++ to Cr++++++	100 to 1000
Copper, Cu++	200 to 4000
Iron, FE++ and Fe+++[c]	100 to 1000
Lead, Pb++	100 to 4000
Magnesium, Mg++	100 to 1000
Manganese, Mn++ to Mn+++++++	100 to 1000
Mercury, Hg+ and Hg++	100 to 1000
Potassium, K+	100 to 1000
Nickel, Ni++	100 to 1000
Silver, Ag+	100 to 1000
Sodium, Na+	100 to 1000
Strontium, Sr++	100 to 1000
Tin, Sn++ and Sn++++	100 to 1000
Zinc, Zn++	100 to 1000

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[a] Volumes specified in this table should be considered as a guide for the approximate quantity of sample necessary for the particular analysis. The exact quantity used should be consistent with the volume prescribed in the standard method of analysis, whenever the volume is specified.

[b] Aliquot may be used for other determinations.

[c] Samples for unstable constituents must be obtained in separate containers, preserved as prescribed, completely filled, and sealed against all exposure.

TABLE 45. SUMMARY OF PRESERVATION METHODS FOR WATER SAMPLES[a] (EPA, 1979a)

Preservative[b]	Action	Applicability
$HgCl_2$	Bacterial inhibitor	Nitrogen forms, phosphorus forms
Acid (HNO_3)	Metals solvent, prevents precipitation	Metals
Acid (H_2SO_4)	Bacterial inhibitor	Organic samples (COD, oil & grease organic carbon), nitrogen-phosphorus forms
	Salt formation with organic bases	Ammonia, amines
Alkali (NaOH)	Salt formation with volatile compounds	Cyanides, organic acids
Refrigeration	Bacterial inhibitor, retards chemical reaction rates	Acidity-alkalinity, organic metals, BOD, color, odor, organic P, organic N, carbon, etc., biological organism (coliform, etc.)

[a] For a more complete list of parameters and associated preservation lists, see EPA, 1979a.

[b] Because of mercury residuals, $HgCl_2$ poses problems in disposal of the sample; research is underway to develop a preservative to replace $HgCl_2$.

monitoring program. These samplers may collect samples over discrete time intervals, or an event such as increased flow volume either in an effluent or a stream may be used to trigger or alter a sampling sequence.

A powerful option with automatic samplers is to combine the sampler with an on-site pollutant monitor. A pollutant associated with the effluent stream of the FBC facility could be monitored continuously. If the pollutant concentration exceeds a predetermined concentration (statistically derived), the sampler would be triggered to collect a sample or series of samples. The data derived from samples collected by such means could be used to monitor pollution abatement equipment efficiency and relate changes in environmental condition to plant operating conditions.

Collecting samples for analysis of trace amounts of organics such as benzo(a)pyrene or fluoranthene often requires different techniques because of large volumes of sample required. These methods normally involve pumping the water to be sampled through an absorbent which is selected to remove the organic pollutant(s) from the water. Commonly used sorbents are XAD resin and granular-activated carbon. The use of these techiques and their application to Level 1/Level 2 analysis has been summarized by Harris and Levins (1978).

Whether manual or automated methods are used to collect samples, a number of parameters in the field should be monitored at the time of sample collection. The parameters which should be measured at time of sampling include: stream flow, temperature, dissolved oxygen, and in the case of lake or ocean sampling, the transparency/visibility.

Since many of the pollutants of interest may be absorbed by particulate matter, sampling of sediment may be required to determine the fate and rate of accumulation of pollutants. The samplers employed may be of two types: 1) traps to collect sediments deposited over a known time period, and 2) grab samplers to collect a profile sample or composite sample. Profile samples may be collected using a core sampler while composite samples may be collected by an Ekman, Ponar or Peterson dredge. The preferred methods of collecting samples for monitoring pollutants discharged in FBC effluent streams are in-place sediment traps and core samplers. Core samplers would be employed to collect samples for analysis of movement of pollutants within the sediments and determination of zones of concentration of pollutants.

Collection of aquatic organisms requires methods similar to those used for sampling sediments. The methods include in-place samplers (artificial substrates) and grab samplers. Numerous types of samplers and methods of collection have been described for various types of organisms (American Public Health Association, 1976; Swartz, 1978; Jacobs and Grant, 1978). For purposes of both substrate and statistical continuity over time, the use of artificial substrates is recommended as the method to be employed for collection of aquatic organisms where such methods are applicable. Artificial substrates are, of course, applicable to sessile organisms, but not to fish or planktonic species.

ANALYTICAL METHODS

Analysis of water samples for collection of water quality data can be achieved in two basic ways. One way is to collect water samples at the desired sampling locations, either manually or with automated sampling apparatus, and transport the samples to a laboratory for analysis. The second way involves the use of on-site and analytical apparatus. In the second method, the analyses are performed in the field automatically, without the aid of an analytical laboratory, except for necessary reagent preparation and required quality assurance checks. Data so collected may be either stored on-site for later retrieval, or transmitted directly to a central data collection point.

Some parameters may be conveniently and accurately measured by on-site monitoring equipment. However, because of the low concentration of many parameters and the presence of interferences, extensive sample preparation is required. This tends to rule out the use of on-site analytical equipment except for a limited number of parameters. Even if the equipment were available to adequately measure concentrations of pollutants with the desired level of accuracy and precision, the cost of the equipment would be prohibitive for more than a very limited number of sampling points.

The level and type of monitoring system or sampling and analytical techniques to be used should always be determined during the developmental stages of the monitoring program, prior to implementation. This will be very important in determining the types of equipment needed, procedures to be used, and the cost of the program.

Approved and Standard Methods

Methods for water quality analysis are varied and widely published. New methods are also continuously being developed and tested. The validity and acceptability of methods for quantitative determination of various water constituents are continuously being reviewed and updated by several organizations. Current editions of the primary reference works are available (EPA, 1979a; American Public Health Association, 1976; American Society of Testing and Materials, 1979).

EPA Form 2350-4 (4-80)
(PREVIOUSLY CIN. EPA FORM 287)
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The EPA has published a list establishing test procedures for the analysis of pollutants as required by Section 304(g) of the Federal Water Pollution Control Act Amendments of 1972 (Federal Register, December 1, 1976). These methods, or approved alternate test procedures, must be used by NPDES permit holders to ensure that effluents meet permit requirements.

Since FBC units and their accessory processes are likely to produce aqueous discharges, the technology would ultimately be regulated by the aforementioned regulations, and therefore EPA-approved methods would be required for at least those parameters for which approved methods are available.

The EPA has expressed concern that the analytical methods used to measure water quality be reliable and reproducible. They suggest the following set of criteria in selecting physical and chemical analytical methods:

- The method should measure the desired constituent with precision and accuracy sufficient to meet the data needs in the presence of the interferences normally encountered in polluted waters.
- The procedure should utilize the equipment and scales normally available in the average water pollution control laboratory.
- The selected methods should be in use in many laboratories or have been sufficiently tested to establish their validity.
- The method should be sufficiently rapid to permit routine use for the examination of large numbers of samples (EPA, 1979a).

EPA-approved analytical methods and additional instrumental techniques for non-metals and metals are given in Tables 46 and 47. Table 48 summarizes the current preferred analytical techniques for the metals. The lack of EPA approval does not reflect a lack of accuracy or precision; in many cases, it indicates a lack of widespread availability of the instrument, a need for highly skilled operators, or high costs associated with operation and/or maintenance.

The selection of analytical techniques to be used in a monitoring program must be based on the needs of the data users and the appropriateness of the techniques available. Table 49 presents a set of criteria for the selection of analytical techniques that are weighted differently for qualitative and quantitative analyses. While the same instrumentation can often be used for both types of analyses, in the

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BOTTOM OF IMAGE AREA OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
PAGE NUMBER
EPA Form 2350-4 (4-80)
[PREVIOUSLY CIN. EPA FORM 287]
U.S. GOVERNMENT PRINTING OFFICE 1980-
TYPING GUIDE SHEET

TABLE 46. STATE-OF-THE-ART WATER QUALITY MONITORING METHODS: NON-METALS

General Physical and Chemical Parameters	EPA-Approved Methods[a]	Other Instrumental Techniques[b]
Acidity	Titrimetric	Colorimetric
Alkalinity	Titrimetric; automated colorimetric	Electrochemical, colorimetric, automated colorimetric
Color	Colorimetric, Spectrophotometric	
Conductivity	Conductance bridge	
Hardness	Titrimetric; automated colorimetric; (Ca + Mg)	Ion selective electrode
pH		Electrochemical
Odor	No EPA method	
Residue, total	Gravimetric 103-105°C	
Residue, total dissolved (filterable)	Glass fiber filtration, 180°C	
Residue, total suspended (nonfilterable	Glass fiber filtration, 103-105°C	
Residue, total volatile	Gravimetric, 550°C	
Settleable Matter	Volumetric or Gravimetric	
Salinity		Conductance
Temperature	Thermometer	Thermistor Thermocouple
Turbidity	Nephelometric	Turbidimeter
Nitrogen, Phosphorus and Sulfur		
Ammonia	Manual or automated colorimetric; titrimetric; electrode	Activation analysis
Nitrate	Manual or automated colorimetric	Activation analysis; UV spectrophotometry
Nitrate	Manual or automated colorimetric	Activation analysis; ion selective electrode
Organic Nitrogen	Total nitrogen minus ammonia	Activation Analysis Automated Colorimetric Colorimetric
Total Nitrogen	Digestion followed by ammonia method	Activation Analysis Automated Colorimetric Colorimetric
Phosphate	Manual or automated colorimetric	
Total Phosphorus	Digestion followed by phosphate method; gas chromatography	
Orthophosphate	Manual or automatic ascorbic acid reduction	
Sulfate	Gravimetric; turbidimetric; automated colorimetric	
Sulfide	Titrimetric; colorimetric	Ion selective electrode
Sulfite	Titrimetric	Colorimetric
Surfactants	Colorimetric (Methylene Blue)	
Dissolved Gases		
Chlorine	Titrimetric; colorimetric	Electrochemical
Hydrogen Sulfide	(none)	Colorimetric; titrimetric
Oxygen	Titrimetric; electrode	

(Continued)

TABLE 46 (Continued)

General Physical and Chemical Parameters	EPA-Approved Methods[a]	Other Instrumental Techniques[b]
Halides and Cyanide		
Fluoride	Ion electrode; manual or automated colorimetric	
Chloride	Titrimetric; automated colorimetric	Ion selective electrode
Bromide	Titrimetric	Colorimetric
Iodide	(none)	Ion selective electrode; colorimetric
Cyanide	Titrimetric; colorimetric	Ion selective electrode
Organic Components		
Total Organic Carbon	Combustion-infrared analysis	Gas & thin layer chromatography; UV spectrophotometry
Petrochemicals	(none)	Gas Chromatography Gas Chromatography/Mass Spectrometry/Computer Thin-Layer Chromatography
Phenols	Colorimetric	Gas Chromatography Thin-Layer Chromatography (Fluorescence) UV Spectrophotometry
Oil & Grease	Gravimetric	Automic absorption; gas & thin layer chromatography; IR and UV spectrophotometry; sensors; reflectance
Chlorinated Organic Compounds	Gas Chromatography	

[a] Federal Register, December 1, 1976.

[b] Lawrence-Berkeley Laboratory, 1976.

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PAGE NUMBER
BOTTOM OF IMAGE AREA OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
EPA Form 2350-4 (4-80)
(PREVIOUSLY CIN: EPA FORM 337)
TYPING GUIDE SHEET

TABLE 47. STATE-OF-THE-ART WATER QUALITY MONITORING METHODS: METALS

Metals	Atomic Adsorption Spectrophotometry	Atomic Emission Spectrophotometry	Atomic Fluorescence Spectrophotometry	Colorimetry	Spark Source Mass Spectrometry	Ion Selective Electrodes	X-Ray Fluorescence	Neutron Activation
Aluminum	E	B		E	B			
Antimony	E							N
Arsenic	E			E				N
Barium	E							N
Beryllium	E	B		E				
Boron	E	B		E				
Cadmium	E	B	B	E		G		N
Calcium	E	B			B	G	B	
Chromium	E	B		E	B		B	N
Cobalt	E							N
Copper	E	B	B	E	B	G	B	N
Gold	E							
Iridium	E							
Iron	E	B	B	E	B		B	N
Lead	E	B		E	B	G	B	
Magnesium	E	B		B	B		B	
Manganese	E	B		E	B		B	N
Mercury	E	B	B					N
Molybdenum	E							
Nickel	E	B		E	B		B	
Osmium	E							
Palladium	E							
Platinum	E							
Potassium	E	E		E	B	B	B	N
Rhodium	E							
Ruthenium	E							
Selenium	E	B		E				N
Silica	B	B		E				
Silver	E	B		B		G		N
Sodium	E	E			B		B	N
Strontium	B	B				B		
Thallium	E							
Tin	E							
Titanium	E	B			B		B	
Vanadium	E	B		E	B		B	
Zinc	E	B		E	B		B	N

KEY: E - EPA-approved guidelines
(Federal Register, December, 1976).

B - Additional instrumental techniques
(Lawrence-Berkeley Laboratory, 1976).

G - Additional techniques such as "unproven sensors"
(U.S. Geological Survey, 1976).

N - Trace metals detectable by neutron activation
(Robertson and Carpenter, 1974).

TABLE 48. ATOMIC ABSORPTION CONCENTRATION RANGES[a]
(EPA, 1979a)

	Direct aspiration			Furnace procedure[b]	
Metal	Detection limit mg/l	Sensitivity mg/l	Optimum concentration range mg/l	Detection limit ug/l	Optimum concentration range ug/l
Aluminum	0.1	1	5 - 50	3	20 - 200
Antimony	0.2	0.5	1 - 40	3	20 - 300
Arsenic[c]	0.002	-	0.002 - 0.02	1	5 - 100
Barium(p)	0.1	0.4	1 - 20	2	10 - 200
Beryllium	0.005	0.025	0.05 - 2	0.2	1 - 30
Cadmium	0.005	0.025	0.05 - 2	0.1	0.5 - 10
Calcium	0.01	0.08	0.2 - 7	-	- -
Chromium	0.05	0.25	0.5 - 10	1	5 100
Cobalt	0.05	0.2	0.5 - 5	1	5 - 100
Copper	0.02	0.1	0.2 - 5	1	5 - 100
Gold	0.1	0.25	0.5 - 20	1	5 - 100
Iridium(p)	3	8	20 - 500	30	100 - 1500
Iron	0.03	0.12	0.3 - 5	1	5 - 100
Lead	0.1	0.5	1 - 20	1	5 - 100
Magnesium	0.001	0.007	0.02 - 0.5	-	- -
Manganese	0.01	0.05	0.1 - 3	0.2	1 - 30
Mercury[d]	0.0002	-	0.0002- 0.01	-	- -
Molybdenum(p)	0.1	0.4	1 - 40	1	3 60
Nickel(p)	0.04	0.15	0.3 - 5	1	5 - 100
Osmium	0.3	1	2 - 100	20	50 - 500
Palladium(p)	0.1	0.25	0.5 - 15	5	20 - 400
Platinum(p)	0.2	2	5 - 75	20	100 - 2000
Potassium	0.01	0.04	0.1 - 2	-	- -
Rhenium(p)	5	15	50 - 1000	200	500 - 5000
Rhodium(p)	0.05	0.3	1 - 30	5	20 - 400
Ruthenium	0.2	0.5	1 - 50	20	100 - 2000
Selenium[c]	0.002	-	0.0002- 0.02	2	5 - 100
Silver	0.01	0.06	0.1 - 4	0.2	1 - 25
Sodium	0.002	0.015	0.03 - 1	-	- -
Thallium	0.1	0.5	1 - 20	1	5 - 100
Tin	0.8	4	10 - 300	5	20 - 300
Titanium(p)	0.4	2	5 - 100	10	50 - 500
Vanadium(p)	0.2	0.8	2 - 100	4	10 - 200
Zinc	0.005	0.02	0.05 - 1	0.05	0.2 - 4

[a] The concentrations shown are not contrived values and should be obtainable with any satisfactory atomic absorption spectrophotometer.

[b] For furnace sensitivity values, consult instrument operating manual; values listed are those expected when using a 20 ul injection and normal gas flow except in the case of arsenic and selenium where gas interrupt is used. The symbol (p) indicates the use of pyrolytic graphite with the furnace procedure.

[c] Gaseous hydride method.

[d] Cold vapor technique.

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TABLE 49. CRITERIA FOR SELECTION OF ANALYTICAL METHODS
(Fennelly et al., 1976)

Requirement	Definition	Relative importance in qualitative analysis	Relative importance in quantitative analysis
Sensitivity	Amount of material that gives a specified response.	High - Being able to "see" any substance on first analysis can save considerable time in later testing.	High - Must be able to "see" at least down to lowest level of concern.
Specificity	Ability to measure only the substance of interest by eliminating interferences.	Low - Detecting even a "hint" of a species is important in screening. Later tests can provide confirmation.	High - Interference can cause erroneous data interpretation.
Precision	Error of the method (often expressed as the coefficient of variation) established by the analysis of many samples containing equivalent amounts of the species of interest.	High - Lack of precision can make a test useless.	High - Lack of precision can make a test useless.
Accuracy	Ability to determine the true value.	Low - An order of magnitude accuracy would be adequate.	High - Should be good to within 100% at parts per billion; 50% at parts per million.
Range of analysis	Concentration range in which reliable results can be obtained.	High - Ideally, a range which spans 10^{-9} to 10^{-3} g-mole/l is desirable.	Low - Screening tests should allow one to preselect optimum range of interest; hence flexibility here is not important.
Stability	Ability of the materials to remain intact over a period of time.	High - Consistency is important in screening tests; instability can also affect precision.	Moderate - One will often have option of selecting optimum time for analysis; hence problems of instability may be avoided.
Ease of handling	Skills required to prepare the sample and execute the analytical methods.	Moderate - Convenience and speed are important in screening tests. Methods requiring advanced skills tend to reduce precision.	Moderate - The importance of the final result should dictate the level of effort.
Response time	Time required to analyze one sample completely.	Moderate - Again convenience is high priority, but low response time could be traded off against ability to measure many different species.	Moderate - Same as in qualitative.
Cost	Actual monetary expenditure for materials, equipment, and personnel needed	Examination of numerous samples requires low cost per sample.	Cost can vary with the importance of the result.
Availability of equipment	Ability to purchase the required equipment and materials needed for an analysis.	High - When many tests are to be performed, one needs easily available supplies.	Moderate - Most important samples can receive special Priority

3/8"
AND ILLUSTRATIONS

former, sensitivity, speed, and ease of performance are most important, while the latter requires precision, accuracy and specificity. The criteria provide guidance concerning the relative importance of each of these factors for both qualitative and quantitative studies.

Since publication of the list of approved methods in the Federal Register (December, 1976), a new edition of "Methods for Chemical Analysis of Water and Wastes" has been published. Some changes in approved analytical methods were made. Atomic absorption is no longer the preferred method for boron, and analysis of rhenium was added as an atomic absorption method.

Trace Organics

As indicated in Table 46, gas chromatography is the preferred method for chlorinated organic compounds and for other trace organic compounds as well. The analysis of organic compounds and development of methods of analysis are under the direction of the Environmental Monitoring and Support Laboratory in Cincinnati with the cooperation of the Environmental Research Laboratory, Athens, Georgia. Gas chromatography-mass spectrometry (GS-MS) methods of analysis have been developed for priority pollutants and for numerous other organics. A partial listing of the organics for which GC-MS methods have been developed is indicated in Table 50. GC-MS methods are preferred when the number of organics to be monitored is more than four or five, or when the actual types of compounds are uncertain. Routine gas chromatography procedures could be used; however, identifying the compounds detected would require additional analytical steps. The additional steps are repetitive analyses of the sample(s) under varying analytical conditions such as different columns, temperature or carrier gas flow rate.

The other major analytical method for measurement of small quantities of organics is high performance liquid chromatography (HPLC). This technique has recently been developed to measure a wide variety of organic compounds, including many of those found in solid wastes and liquid effluents that may be byproducts of FBC technology.

Biological Methods

The biological methods useful in providing information for assessment of environmental impacts of FBC effluents may include any of several methods depending on the nature and quality of a receiving water, the objectives of the program and the funds available. The basic types of biological assay methods are:

TABLE 50. ORGANICS FOR WHICH DISCRETE ANALYTICAL METHODS (GC-MS) HAVE BEEN DEVELOPED
(EPA, 1977b)

1, 3-dichlorobenzene
1, 4-dichlorobenzene
hexachloroethane
1,2-dichlorobenzene
bis (2-chloroisopropyl) ether
hexachlorobutadiene
1,2,4 trichlorobenzene
naphthalene[a]
bis (2-chloroethyl) ether
hexachlorocyclopentadiene
nitrobenzene
bis (2-chloroethoxy) methane
2-chloronaphthalene
acenaphthylene
acenaphthene
isophorone
fluorene
2,6-dinitrotoluene
1,2-diphenylhydrazine
2,4-dinitrotoluene
N-nitrosodiphenylamine
hexachlorobenzene
4-bromophenyl phenyl ether
phenanthrene[a]
anthracene[a]
dimethylphthalate
diethylphthalate
fluoranthene[a]
pyrene[a]
di-n-butylphthalate
benzidine
butyl benzylphthalate
2-chlorophenol
phenol
2, 4-dichlorophenol
2-nitrophenol
p-chloro-m-cresol
2,4,6-trichlorophenol
2,4-dinitrophenol
2,4-dimethylphenol
4,6-dinitro-o-cresol
4-nitrophenol
pentachlorophenol
chrysene[a]
bis(2-ethylhexyl)phthalate
benzo(a)anthracene[a]
benzo(b)fluoranthene[a]
benzo(k)fluoranthene[a]
benzo(a)pyrene[a]
indeno(1,2,3-cd)pyrene[a]
dibenzo(a,h)anthracene[a]
benzo(g,h,i)perylene[a]
N-nitrosodimethylamine
N-nitrosodi-n-propylamine
4-chloro-phenyl phenyl ether
endrin aldehyde
3,3'-dichlorobenzidine
2,3,7,8-tetrachlorodibenzo-p-dioxin
bis(chloromethyl)ether
deuterated anthracene (d10)

---

[a] Indicates organics measured for or detected in FBC effluent streams.

- Determination of biomass
- Identification and enumeration of organisms collected from the aquatic system
- Determination of toxicity of effluents to test organisms
- Determination of mutagenicity and cytotoxicity

Biomass determinations are useful in measuring growth rates of aquatic organisms in relation to responses induced by pollutants discharged from a particular source. Methods for measuring biomass have been summarized by Weber (1973) and Cairns and Dickson (1973). Generally, when biomass determinations are made, identification of at least the dominant types of organisms present are also done. The conventional method of measuring biomass is to weigh the collected organisms, and express the mass as dry weight, or ash-free dry weight per unit area or volume of the environment from which the sample was taken. Instrumental methods applicable to measurement of biomass include determination of chlorophyll and adenosine triphosphate.

Identification and enumeration of organisms and analysis of the resultant data by any of several biotic or species diversity indices should be specified. Methods of collection, and identification of organisms, and use and interpretation of indices have been documented (Dalton·Dalton·Newport, 1978). Because of the wide variety of collection methods, organism identification aids, and methods of interpretation of the data, the EPA should recommend acceptable complementary methods. The recommended methods could then be employed for analysis of impacts of FBC effluents upon surface waters for those pilot and demonstration-scale plants where such methods would be applicable.

The methods for testing the toxicity of effluents to aquatic organisms and determining mutagenicity and cytotoxicity have been adequately described (Cairns, et al., 1976; Duke et al., 1977; Peltier, 1978; Dalton·Dalton·Newport, 1978) and are not repeated here. The EPA should vigorously apply these methods to testing of effluents from FBC units, particularly the long-term tests. It would also be desirable to compare test results of FBC effluents with results of tests of conventional coal combustion effluents to obtain a measure of the relative hazard of each technology.

Level 1/Level 2 Analysis

Investigations are currently underway to determine the exact nature and composition of the effluents of the FBC process, how they might affect the environment or react to environmental conditions, and the fate of the individual pollutants or classes of pollutants in the environment. The methods used to identify and quantify the pollutants in the effluent streams of the FBC technology are based on the phased approach to sampling and analytical strategy (Dorsey et al., 1977). The phased approach has three levels of effort for determining what parameters should be monitored for the FBC technology (Harris and Levins, 1978):

- Level 1 Assessment
  - provides preliminary environmental assessment data
  - identifies principal problem areas
  - provides the data needed for priority ranking of energy and industrial processes, components within a waste stream, and classes of materials for further consideration in the overall assessment
- Level 2 Assessment
  - provides additional information that will confirm and expand the information gathered in Level 1 assessment
  - defines control technology needs and in some cases provides the probable or exact cause of a given problem.
- Level 3 Assessment
  - uses sampling and analytical methods whose precision and accuracy are sufficient to permit quantitative monitoring of specific pollutants identified in Level 2 assessment
  - may be used in the design and development of suitable pollution control devices

All three assessment levels are appropriate for application to commercial-scale operation of an FBC coal boiler. Whether or not a particular level of assessment is used depends on the amount of information available concerning the energy technology.

Specific methodologies have been described for Level 1 and Level 2 analysis (Lentzen et al., 1978; Ryan et al., 1979; Harris et al., 1979). Thus far, the major emphasis in utilization of the methods has been directed toward their full development. When the methods have been fully developed, they can be applied to pilot and demonstration-scale FBC units to determine scale-up factors for effluents and pollutants from commercial-scale FBC units. The limitations on use and degree of uncertainty of the Level 1/Level 2 data must, of course, also be determined.

The quality assurance requirements for ambient monitoring programs are outlined in Appendix A. The guidelines are also applicable to other types of monitoring such as effluent monitoring and the type of monitoring performed using Level 1/Level 2 methodologies. A specific guideline (Smith, 1978) has been developed for Level 1 analysis which specifies the degree of quality assurance required.

Data Recording

Data recording is basically the transfer of new data generated during analysis into a form which will allow its future use. The data obtained from meter dials, vernier, digital displays or other devices may be recorded manually or obtained from automatic data loggers or from computer interfaces.

In general, two steps are involved in data recording. The first involves transfer of new data to either laboratory or field notebooks or to raw data forms. Some analytical equipment such as automatic field monitors and automated laboratory equipment may feed data directly to a computer for both storage and performance of additional calculations such as statistics for the data and eventual printout of data summaries. In this step all operational parameters, methods, deviation and results are recorded, and calculations performed.

The second step involves transfer of the data generated during the laboratory or field analysis into a format which is useful during data analysis. The data from Level 1/Level 2 analysis may be transferred to the forms developed for SAM 1A (Schalit and Wolfe, 1978) or to a similar format. Ambient monitoring data may be transferred to forms similar to the 305b Reports, currently an EPA requirement for state monitoring networks.

DATA HANDLING

The chief purpose of prescribing data handling procedures is to assure that data reach the appropriate personnel. The data may be used for interpretation of plant operating conditions, to determine impacts upon water quality, to generate information useful for designing wastewater treatment facilities, or for enforcement activities. However, data cannot serve any useful function unless they reach the appropriate personnel.

Data may be obtained from three basic sources in an ambient monitoring program: 1) samples taken to a laboratory

EPA Form 2350-4 (4-80)
(PREVIOUSLY CIN. EPA FORM 237)
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TYPING GUIDE SHEET

for analysis, 2) automatic field analyzers, or 3) sources outside the program such as USGS monitoring programs or state/local ambient monitoring programs. Whatever their source, the data must be either initially put into a format or transcribed into a format consistent with those required by data processing and data analysis procedures. The format will normally be a preprinted form which contains spaces for all information pertinent to the data or their interpretation. Figure 34 describes the flow of data in an ambient monitoring program. At each step in the data flow process where information is produced, collated or changed in form, a quality assurance check must be performed to assure that no errors are introduced and that any errors are within acceptable limits.

Whenever data are transmitted via telemetry or other devices, priorities must be established. The considerations include the critical need for the data in a proper time frame, and the ability of the various transmission systems to accomplish the task with accurate understanding of the time and cost requirements. The quality assurance of various transmission systems must also be evaluated, and the ability to incorporate feedback mechanisms is of prime importance.

The ambient monitoring programs operated in conjunction with development and implementation of commercial-scale FBC facilities are likely to be financed either directly or indirectly by the EPA. The data produced by ambient monitoring programs should therefore be available on call in acceptable format. The STORET system should be employed to receive information produced in the monitoring programs. It may also be desirable to store pertinent data on in-house computer banks at the various EPA facilities which are engaged in coordinating energy/environment research activities. This would allow personnel responsible for decision making to have immediate access to information required for adequate and responsible decisions.

Other data banks that can be used to store data generated during the ambient monitoring programs and to obtain useful information include the National Water Data Exchange (NAWDEX) which is operated by the U.S. Geological Survey. Table 51 summarizes the data systems which participate in NAWDEX.

Data dissemination means that data are reaching the personnel who are responsible for utilizing the data whether for research purposes, enforcement activities or preparation of special reports. Each level of operation in the ambient monitoring program must be supplied with a list of individuals and organizations who are to receive information with the type and format of that information specified. Data handling and

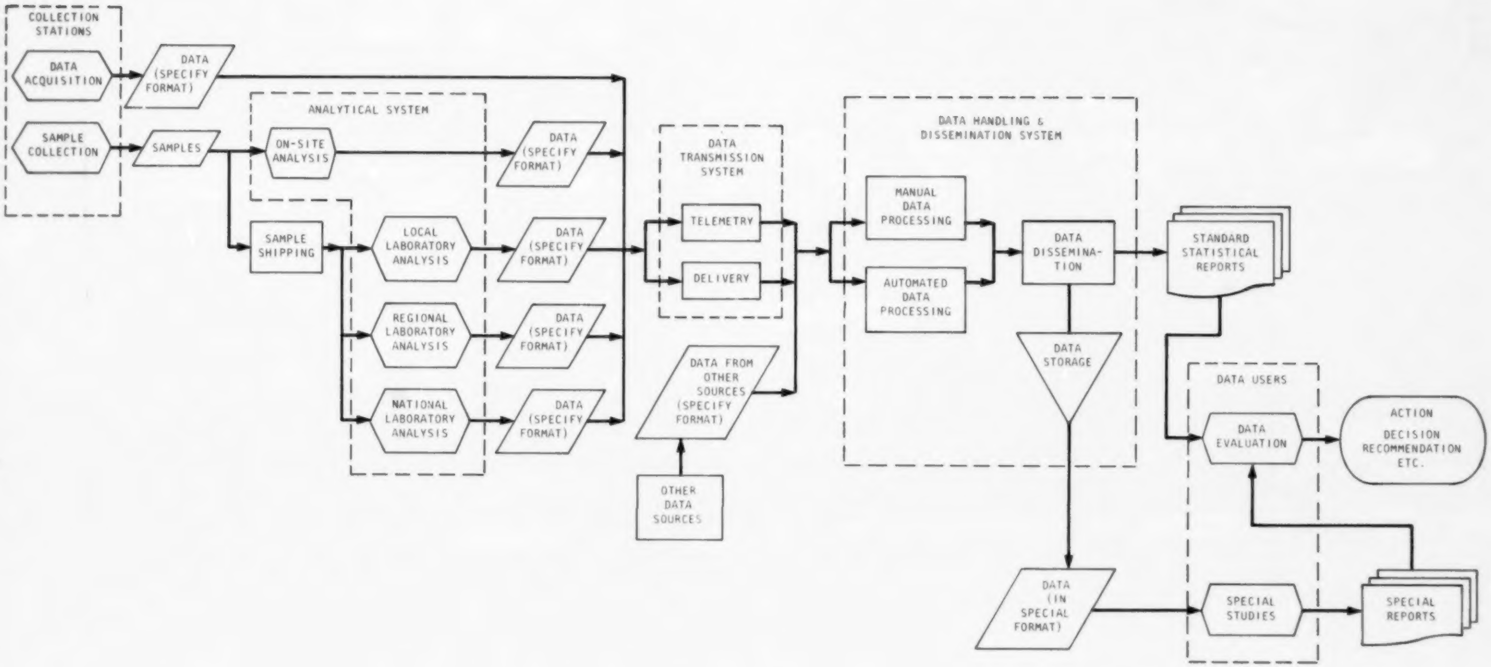
COLLECTION STATIONS
DATA ACQUISITION
SAMPLE COLLECTION
DATA (SPECIFY FORMAT)
SAMPLES
ANALYTICAL SYSTEM
ON-SITE ANALYSIS
SAMPLE SHIPPING
LOCAL LABORATORY ANALYSIS
REGIONAL LABORATORY ANALYSIS
NATIONAL LABORATORY ANALYSIS
DATA (SPECIFY FORMAT)
DATA (SPECIFY FORMAT)
DATA (SPECIFY FORMAT)
DATA (SPECIFY FORMAT)
DATA TRANSMISSION SYSTEM
TELEMETRY
DELIVERY
DATA FROM OTHER SOURCES (SPECIFY FORMAT)
OTHER DATA SOURCES
DATA HANDLING & DISSEMINATION SYSTEM
MANUAL DATA PROCESSING
AUTOMATED DATA PROCESSING
DATA DISSEMINA-TION
DATA STORAGE
DATA (IN SPECIAL FORMAT)
STANDARD STATISTICAL REPORTS
DATA USERS
DATA EVALUATION
SPECIAL STUDIES
ACTION DECISION RECOMMENDATION ETC.
SPECIAL REPORTS

Figure 34. Data flow in a source-oriented ambient monitoring program.

(NUS Corporation, 1970)

TABLE 51. NAWDEX PARTICIPATING DATA SYSTEMS
(Edwards, 1978)

Name of System	Organization	Location	Type of System
National Water Data Storage and Retrieval System (WATSTORE)	U.S. Geological Survey	Reston, VA	Water data
Storage and Retrieval System (STORET)	U.S. Environmental Protection Agency	Washington, DC	Water quality data
Water Resources Scientific Information System (WRSIC)	Office of Water Research and Technology, U.S. Dept. of Interior	Washington, DC	Water-related bibliographic references
Environmental Data Index (ENDEX)	Environmental Data and Information Service, NOAA	Washington, DC	Index of environmental data files
Oceanic and Atmospheric Scientific Information System (OASIS)	Environmental Data and Information Service, NOAA	Washington, DC	Environmental bibliographic references
National Climatic Center (NCC)	Environmental Data and Information Service, NOAA	Asheville, NC	Meteorological data
National Oceanographic Data Center (NODC)	Environmental Data and Information Service, NOAA	Washington, DC	Oceanographic data
Environmental Science Information Center (ESIC)	Environmental Data and Information Service, NOAA	Washington, DC	Environmental data
Center for Climatic and Environmental Assessment (CCEA)	Environmental Data and Information Service, NOAA	Columbia, MO	Climatic impacts on the environment
Center for Experiment Design and Data Analysis (CEDDA)	Environmental Data and Information Service, NOAA	Washington, DC	Oceanographic and atmospheric data
National Geophysical and Solar Terrestrial Data Center	Environmental Data and Information Service, NOAA	Boulder, CO	Seismology, marine geology and geophysics, geomagnetism, solar activity, interplanetary phenomena

(Continued)

TABLE 51 (Continued)

Name of System	Organization	Location	Type of System
Water Resources Document Reference Centre (WATDOC)	Inland Waters Directorate, Canadian Department of Fisheries and the Environment	Ottawa, Canada	Water-related bibliographic references
Texas Natural Resources Information System (TNRIS)	Texas Natural Resources Information System	Austin, TX	Water and environmental data
Iowa Water Resources Data System (IWARDS)	Iowa Geological Survey	Iowa City, IA	Water data
Nebraska Natural Resources Information System	Nebraska Natural Resources Commission	Lincoln, NE	Water and environmental data
Water Resources Data System	Pennsylvania Department of Environmental Resources	Harrisburg, PA	Water data
REAP Resources Reference System	North Dakota Regional Environmental Assessment Program	Bismarck, ND	Water and environmental data
Colorado Water Data Bank (CWDB)	Colorado Division of Water Resources	Denver, CO	Water data
Snow Telemetry System (SNOTEL)	Soil Conservation Service	Portland, OR	Hydrometeorological data
Water Supply Data Base	Electric Power Research Institute	Palo Alto, CA	Index of water data systems
Great Lakes Regional Information Referral Center	Great Lakes Basin Commission	Ann Arbor, MI	Water resources of the Great Lakes

dissemination systems are the final step in placing data into a proper framework for use.

DATA ANALYSIS

Data analysis techniques are used to derive information from data acquired in an ambient monitoring program, e.g.,

- Screen basic data to set priorities for pollutant or parameter selection.
- Provide information concerning the quality of the data produced.
- Determine variables important in determining changes in water quality.
- Relate changes in water quality to the source of the pollutants and changes in concentration of the source.

Analysis techniques may range from simple measures of data quality such as standard direction to complex water quality models. The methods available include:

- Regression Analysis
- Time-Trend Analysis
- Factor Analysis
- Water Quality Indices
    - Chemical
    - Biological
- Water Quality Model

Regression Analysis

Using regression analysis, a single variable of interest can be expressed as a function of the concentration of one or more different (independent) variables (pollutants). For example, if the concentration of a pollutant such as benzo(a)pyrene were shown to be related to the concentration of a more easily measured parameter such as nitrite or sulfite, by measuring the concentration of nitrite or sulfite, the concentration (within certain statistical limits) of benzo(a)pyrene can be calculated. If predictive functions can be developed relating dependent variables such as benzo(a) pyrene to one or more easily independent variables, the need to measure dependent variables decreases and the costs of monitoring may also decrease. As long as the functional relationship of variables is valid, and the errors of the estimates of the dependent variables made in this manner are within acceptable limits, only independent variables need to be monitored (Ward, 1979).

While the form of the analysis should be kept simple, prediction capabilities can be improved by adding more independent variables or changing independent variables to produce a usable water quality model. With more variables, the model may represent a set of conditions unique to the data set used for the determination.

Time Trend Analysis

Water quality, the pollutants present in the water, and the pollutants that can be in the water vary with diurnal, seasonal, or yearly fluctuations. Long-term changes in water quality must be distinguished from short-term changes. This requires consistent sampling and methods over time for all variables. It has been demonstrated that trend analyses are better performed on harmonic-analysis coefficients rather than on statistical measures based on the data themselves (Steele and Dyar, 1974). While this method may not be directly applicable to source-oriented ambient monitoring, it can be useful in determining the state of water quality during the period of obtaining background data. Once the state of water quality and variation therein are determined, changes in water quality induced by a particular source of pollutants can be more easily determined.

Factor and Principal Component Analysis

The general goal of factor analysis is the reduction of a set of basic data variables to a smaller set of new uncorrelated variables which are defined solely in terms of the original data, and retain the most important information contained in the original data (Ward, 1979). These analytical procedures (described by Veldman, 1967) can be used to identify means of achieving cost-effective monitoring networks by reduction of some water quality variables.

Principal-component analysis is one of a number of factor extraction methods. The factor-loading matrix obtained from a principal-component analysis reflects the characteristics of the extraction procedure, which maximizes the variance in each succeeding column of the matrix. The first principal component is easily interpreted and requests the central focus of a set of original variables (Ward, 1979). In many water quality studies utilizing factor analysis and principal component analysis (Daudy and Feth, 1967; Symader and Thomas, 1978; Hermann et al., 1979), explanations for observed component loadings were developed and sets of variables were identified that tended to behave together in terms of spatial or temporal variability (Ward, 1979).

Water Quality Indices

Water quality indices are of two basic types. Those that aggregate a set of different chemical parameters to arrive at a single number which describes the water quality at a specific point in time and space are chemical water quality indices. Biological water quality indices aggregate biological data (e.g., numbers of benthic macroinvertebrates).

Many chemical water quality indices and their uses have been described (Ott, 1978). The number of parameters that have been incorporated into a chemical water quality index has ranged as high as 31 (Stoner, 1976), but the normal range is 8 to 14. The parameters most frequently incorporated in indices are those which are associated with organic pollution, nutrients, and effects of high levels of nutrients, although the same parameters may be equally associated with natural nutrient loading conditions.

Water quality indices are used primarily to derive quantitative measures that can be understood and used by laymen and water resource planners (Landwehr, 1974). In many indices, the individual parameters are weighted with regard to their relative importance in determining water quality, and each parameter has a unique mathematical relationship to water quality. The weighting system and the relationship to water quality may be derived from subjective or objective analysis, with the latter employing the statistical methods described earlier.

Increases in many pollutants (individually or in combination from a particular source) will alter the stability of the ecosystem (including its chemical stability), causing changes in the biotic system and alterations in the chemical system. These changes in chemical structures may be monitored by an "indicator parameter" and mathematically presented in the form of an index value. When a specific index is used, both the parameters employed and the sampling and analytical methods must remain consistent throughout the monitoring program, unless it can be demonstrated that other methods produce the same data.

Aquatic organisms tend to integrate all the stresses placed on the aquatic system and reflect the combined effects over extended periods of time (Landwehr, 1974). Using this principle, "biotic indices" have been derived to produce a single number which represents the water quality at a given location and point in time. The indices in common use are of two general types. One type segregates aquatic organisms into class according to their sensitivity to "pollution" and derives a ratio based on the number of organisms in each class to the total number of organisms (Scott, 1969; Chutter, 1972; Brinkhurst et al., 1968). A second common type of index, based on information theory (Pielou, 1966; Wilhm, 1967; Wilhm, 1970), includes diversity and ordination indices. Rather than being based on information denoted by a single class of organism, these indices are based on information contained in the entire aquatic community or some segment thereof. Generally, both indices utilize benthic macroinvertebrates as the indicator group of organisms, although fish, algae and other types of organisms have been employed.

Biotic indices may be very useful in determining long-term environmental impacts of particular pollutants upon the aquatic ecosystem. However, since the organisms will respond to the sum total of pollutants present, the specific usefulness of these methods will be reduced in direct correlation to the number of sources of pollutants.

Water Quality Models

Three types of water quality simulation models have been employed by various investigations. These are:

- Steady State - Non-Dispersive
- Steady State - Dispersive
- Time Variant

Most of the applications of these models involve waste load allocation of major pollutants, and are not directly applicable to determining effects of highly toxic micropollutants. They are useful, however, in determining the potential distribution of pollutants in the aquatic environment, particularly if the FBC facility discharges to a lake or ocean. The use of such models may be necessary in large bodies of water to determine the distribution of pollutants, and the most desirable or cost-effective locations for sampling.

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SECTION 6

CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS

Based on currently available information, FBC of coal is a more efficient and less environmentally damaging way of extracting coal energy than conventional pulverized coal combustion. As an energy technology, FBC is a subcategory of coal combustion processes, and therefore, is subject to the same technical criteria and standards applicable to coal-fired facilities of similar size and application.

Although a substantial data base has been developed on FBC processes, most of the environmental data have been generated from bench scale and pilot plant units. The data have significant gaps on the chemical profiles of effluents generated during different operating conditions. Most of the data base on effluent characterization was generated from research projects. The extrapolation of such data to commercial-scale FBC units cannot be done with any accuracy. In this study we have treated the research data as "worst case" for any FBC unit, without introducing any dilution factors when calculating emission rates and quantities of pollutants. At this time this approach is the most acceptable alternative.

Based on the best projections for commercialization of FBC processes, the environmental characterization programs for this technology are not current. Efforts directed towards environmental characterization are research-oriented, and the results cannot be readily applied to commercial-scale facilities. In addition, the research data are difficult to obtain and are not part of any readily accessible environmental information system.

RECOMMENDATIONS

Recommendations for additional research and future monitoring of FBC units are:

- Level 1/Level 2 analytical methodologies should be applied to plants larger than the bench scale units that have been used to demonstrate the phased approach techniques, including units exceeding 200 megawatts in power output.

- Sulfur compound speciation testing in Level 1/Level 2 analysis should be conducted on all atmospheric and fugitive emission streams.

- Level 1 biological testing procedures should be utilized on liquid, solid and gaseous effluents (Lentzen et al., 1978).

- Effluent streams that are generated during start-up and shutdown cycles of both the Atmospheric and Pressurized FBC unit should be tested. This effort should be directed towards units larger than the bench scale units that have been used to generate the currently available Level 1/Level 2 information.

- Effluent streams should be monitored, particularly bed reject material, flue gas particulates, and gaseous emissions during combustor unit upset conditions. The latter condition should include:
  - Substantial changes in flow rate of air to the combustor
  - Changes in feed rate of coal and sorbent
  - Both increases and decreases in combustor operating temperature

  The upset conditions should be artificially generated on combustor units initially operating at steady state conditions.

- Bed reject material and other FBC solid wastes generated during normal and upset operating conditions should be tested for their ability to release toxic or other environmentally injurious substances when disposed of in landfills individually, when mixed, and in combination with solid wastes from other sources. Suggested types of solid wastes which should be tested with FBC wastes include:
  - Flue gas desulfurization wastes
  - Bottom ash from conventional coal-fired combustors
  - Municipal and commercial incinerator wastes
  - Sludge and other solid wastes from municipal and other wastewater treatment plants
  - Other types of solid wastes listed as "special wastes" under proposed RCRA regulations
  - Other solid wastes with which FBC wastes might not be compatible, but which could be disposed of in the same landfill

- Plume transformation studies should be conducted on large FBC facilities such as the proposed TVA 200 megawatt plant.

- The IERL-RTP data storage system should be used to store data relating to all FBC process, analytical, and environmental information. This information should be readily available to EPA planners, decision makers and contractors.

- Sufficient data should be generated on conventional coal combustion units to make a complete comparison of environmental impacts of the effluents generated by the two processes, not simply to compare the relative amounts of sulfur dioxide and nitrogen dioxide produced.

- Potential impacts from wastes generated by and resulting from the sorbent regeneration process should be investigated, to determine:
    - The fate of pollutants concentrated in bed reject material during the sorbent regeneration process.
    - The chemical composition of sorbent material when the useful life of the material has been reached.
    - The leachate composition of the spent sorbent and comparisons of leachate characteristics to that of once through bed reject material.
    - The leachate quality when spent sorbent is mixed with other FBC solid wastes, and investigation into compatibility for disposal with other types of solid wastes.
    - The nature, composition, and quantities of liquid, atmospheric, and fugitive emissions from the sorbent regeneration and allied sulfur recovery processes.

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REFERENCES

Abelson, H.I., and W.A. Lowenbach. 1977. Procedures Manual for Environmental Assessment of Fluidized-Bed Combustion Process. EPA-60017-77-009, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.

Allen, J.M., J.E. Howes, Jr., S.E. Miller, and K.M. Duke.
1978a. Comprehensive Analysis of Emissions for EXXON Fluidized-Bed Combustion Miniplant Unit. In Compilation of Level 1 Environmental Assessment Data, eds. N.H. Gaskins and F.W. Sexton. EPA-600/2-78-211, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.

1978b. Comprehensive Analysis of Emissions from MERC Fluidized-Bed Combustion Unit. In Compilation of Level 1 Environmental Assessment Data, eds. N. H. Gaskins and F.W. Sexton. EPA-600/2-78-211, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.

Alvin, M.A., E.P. O'Neill, and D.L. Keairns. 1977. Thermodynamic Projections of Trace Element Release in Fluidized- Bed Combustion Systems. Proceedings of the Fifth International Conference on FBC, Volume 2. The Mitre Corporation, Washington, D.C.

Alvin, M.A., E.P. O'Neill, L.N. Yannopoulos, and D.L. Keairns. 1978. Evaluation of Trace Element Release from Fluidized- Bed Combustion Systems. EPA-600/7-78-050, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.

American Public Health Association. 1976. Standard Methods for the Examination of Water and Wastewater, 14th Edition. American Public Health Association, Washington, DC.

American Society for Testing and Materials. 1979. Annual Book of ASTM Standards, Part 31 - Water. American Society for Testing and Materials, Philadelphia, Pennsylvania.

Anderson, L.B., M.A. Herther, and R.J. Milligan. 1978. SAM 1: An Intermediate Screening Method for Environmental Assessment of Fossil Energy Process Effluents. Acurex Report TR- 79-154.

Andren, A.W., D.H. Klein, and Y. Talmi. 1975. Selenium in Coal- Fired Steam Plant Emissions. Environmental Science and Technology, 9(9): 856.

Babcock & Wilcox Company. 1979. FBC Development Facility and Commercial Utility AFBC Design Assessment. Technical Progress Report No. 8, Electric Power Research Institute, Palo Alto, California.

Ball, R.J., and G.E. Anderson. 1977. Optimum Site Exposure Criteria for SO_2 Monitoring. The Center for the Environment and Man, Inc., Hartford, Connecticut. (EPA-450/3-77-013.)

Beer, J.M., A.F. Sarofim, L.K. Chan, and A.M. Sprouse. 1977. NO Reduction by Char in Fluidized Combustion. Proceedings of Fifth International Conference on FBC, Volume 2. The Mitre Corporation, Washington, DC.

Behar, J. V., E. A. Schuck, R. E. Stanley, and G. F. Morgan. 1979. Integrated Exposure Assessment Monitoring. Environmental Science and Technology, 13(1):34-39.

Branson, D.R. 1978. Predicting the Fate of Chemicals in the Aquatic Environment from Laboratory Data. In Estimating the Hazard of Chemical Substances to Aquatic Life, eds. John Cairns, Jr., K.L. Dickson, and A.W. Maki. ASTM STP 657, American Society for Testing and Materials.

Brinkhurst, R.O., A.L. Hamilton, and H.B. Herrington. 1968. Components of the Bottom Fauna of the St. Lawrence Great Lakes. Publication No. 33, Great Lakes Institute, University of Toronto.

Cairns, J., and K.L. Dickson. 1973. Biological Methods for the Assessment of Water Quality. ASTM Special Publication 528, American Society for Testing and Materials, Philadelphia, Pennsylvania.

Cairns, J., K.L. Dickson, and G.F. Westlake. 1976. Biological Monitoring of Water and Effluent Quality. ASTM Special Technical Publication 607, American Society for Testing and Materials, Philadelphia, Pennsylvania.

Cairns, J., and A.W. Maki. 1979. Hazard Analysis in Toxic Materials Evaluation. Journal of the Water Pollution Control Federation, 51(4):666-671.

Carpenter, R.L., S.H. Weissman, G.J. Newton, R.L. Hanson, E.R. Peele, M.H. Mazza, J.J. Kovach, D.A. Green, and U. Grimm. 1978. Characterization of Aerosols Produced By an Experimental Fluidized Bed Coal Combustor Operated with Sub- Bituminous Coal. LF-57, Lovelace Biomedical and Environmental Research Institute, Albuquerque, New Mexico.

Chemical and Engineering News. 1978. Power Plant Ash Disposal a Growing Problem. Chemical and Engineering News, 56(45):26.

Chutter, F.M. 1972. An Empirical Biotic Index of the Quality of Water in South African Streams and Rivers. Water Research, 6:19-30.

Cleland, J.G., and G.L. Kingsbury. 1977. Multi-media Environmental Goals for Environmental Assessment, Volumes 1 and 2. EPA-600-77-136a and 136b, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.

Coherd, C., and T. Cusino. 1979. Development of Emission Factors for Wind Erosion of Aggregate Storage Piles. 72nd Annual Meeting of the Air Pollution Control Association, Cincinnati, Ohio.

Conner, W.D. 1979. Comparative Study of Plume Opacity Measurement Methods. U.S. Environmental Protection Agency, Stationary Source Emission Measurement Research Branch, Research Triangle Park, North Carolina.

Conner, W.D., and J.R. Hodkinson. 1972. Optical Properties and Visual Effects of Smoke-Stack Plumes. Publication Number 999-AP-30, U.S. Public Health Service, Washington, DC.

Cornaby, B.W., D.A. Savitz, L. Pomerantz, and K.S. Murthy. 1977. Development of Environmental Objectives Based on Health and Ecological Effects. Proceedings of the Fifth International Conference on Fluidized Bed Combustion, Volume 2. The Mitre Corporation, Washington DC.

Couch, D.B., N. L. Forbes, and A.W. Hsie. 1978. Mutation Research 57, 217.

Dalton·Dalton·Newport. 1978. Guidelines for Multimedia Environmental Monitoring of DOE Fossil Energy RD&D Facilities, Volumes 1 and 2. Dalton·Dalton·Newport, Cleveland, Ohio. (NTIS No. FE-2495-6 A01.)

Daudy, D.R., and J.H. Feth. 1967. Applications of Factor Analysis in a Study of Chemistry of Groundwater Quality, Mojave River Valley, California. Water Resources Research, 3(2):505-510.

DeAngelis, D.G., and R.B. Reznik. 1979. Source Assessment: Residential Combustion of Coal. EPA-600/2-79-019a, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.

Denver Research Institute. 1979. Balloon Plume Sampler. Technical Progress Report, University of Denver, Denver, Colorado.

Donahue, J. M. 1970. Chemical Treatment. Industrial Water Engineering, 7(5):35.

Dooley, J.C. 1976. Fumigation From Power Plant Plumes in the Lakeshore Environment. University of Wisconsin-Milwaukee, Milwaukee, Wisconsin.

Dorsey, J.A., L.D. Johnson, R.A. Statnick, and C.H. Lockmuller. 1977. Environmental Assessment Sampling and Analysis: Phased Approach and Techniques for Level 1. EPA-600/2-77- 115, U.S. Environmental Protection Agency, Industrial Environmental Research Laboratory, Research Triangle Park, North Carolina.

Draggan, S., and J. M. Giddings. 1978. Testing Toxic Substances for Protection of the Environment in the Science of the Total Environment, Volume 9. Amsterdam: Elserrier Scientific Publishing Co.

Druckrey, H., H. Kruse, R. Preussmann, S. Ivankovic, and C. Landshutz.
1966. Z. Krebsforsch 68, 103.

1970. Z. Krebsforsch 74, 241.

Duke, K.M., M.E. Davis, and A.J. Dennis, 1977. IERL-RTP Procedures Manual: Level 1 Environmental Assessment Biological Tests for Pilot Studies. EPA 600/7-77-043, U.S. Environmental Protection Agency, Industrial Environmental Research Laboratory, Research Triangle Park, North Carolina.

Dybdahl, A.W., and M.J. Cunningham. 1979. Utilization of the Omega-I Lidar in EPA Enforcement Activities. Symposium on the Transfer and Utilization of Particulate Control Technology, National Enforcement Investigations Center, Denver, Colorado.

Eatough, D. J. 1979. Determination of Sulfur Speciation in Industrial Aerosols in an SO_2 Rich Environment - Summary Progress Report for Period 15 June 1976 - 14 June 1979 (DOE Contract EY-76-S-02 2988). U.S. Department of Energy, Thermochemical Institute, Brigham Young University, Provo, Utah.

Edwards, M.D. 1978. NAWDEX - A Program to Improve Access to Water Data. Water Resource Division, U.S. Geological Survey. Presented at National Conference on Quality Assurance, Denver, Colorado.

Eimutis, E.C. 1976. Source Assessment: Prioritization of Stationary Air Pollution Sources - Model Description. EPA- 600/2-76-032a, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.

Ensor, D. S., and J. J. Pilat.

1970. Plume Opacity and Particulate Mass Concentration. Atmospheric Environment, 4: 163-173.

1971a. Calculation of Smoke Plume Opacity from Particulate Air Pollutant Properties. Journal of the Air Pollution Control Association, 21:496-501.

1971b. Comparison Between the Light Extinction Aerosol Mass Concentration Relationship of Atmospheric and Air Pollutant Aerosols. Atmospheric Environment, 5:209-215.

Environment Reporter. 1979. EPA Initiates Testing To Evaluate Dioxins Created by Natural Combustion. Environment Reporter, 10(18):1077.

Everett, L.G., ed. 1979. Groundwater Quality Monitoring of Western Coal Strip Mining: Identification and Priority Ranking of Potential Pollution Sources. EPA -60017-79-024, Research Triangle Park, North Carolina.

Everett, L.G., K. D. Schmidt, R. M. Tinlin, and D. K. Todd. 1976. Monitoring Groundwater Quality: Methods and Costs. EPA-600/4-76-023, U. S. Environmental Protection Agency, Office of Research and Development.

Exton, R.J. 1977. An Ultraviolet Video Technique for Visualization of Stack Plumes and for Measuring Sulfur Dioxide Concentration and Effluent Velocity. Technical Paper 1014, National Aeronautics and Space Administration, Hampton, Virginia.

Farmer, M.H., E.M. Magee, and F.M. Spooner. 1977. Application of Fluidized-Bed Technology to Industrial Boilers. EPA- 600/7-77-011, U.S. Environmental Protection Agency, Industrial Environmental Research Laboratory, Research Triangle Park, North Carolina.

Federal Power Commission.

1974a. Electric Power Statistics. U.S. Department of Commerce, Washington, D.C.

1974b. Steam Electric Plant Air and Water Quality Control Data for the Year Ended December 31, 1971. FPC-S- 239, U.S. Department of Commerce, Washington, D.C.

Federal Register.

12-1-76. EPA-Approved Guidelines Establishing Test Procedures for the Analysis of Pollutants. Federal Water Pollution Control Act Amendments of 1972, Section 304(g), 40 CFR 136(41 FR 52780).

5-10-79. Ambient Air Quality Monitoring, Data Reporting, and Surveillance Provisions. 40 CFR 51, 52, 53, 58.

Fennelly, P.F., D.F. Durocher, H. Klemm, and R.R. Hall. 1977. Preliminary Environmental Assessment of Coal-Fired Fluidized-Bed Combustion Systems. EPA-600/7-77-054, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.

Fennelly, P.F., D.F. Durocher, A.S. Werner, M.T. Mills, S.M. Weinstein, A.H. Castaline, and C. Young. 1976. Environmental Assessment Perspectives. GCA Corporation, Bedford, Massachusetts. (EPA-600/2-76-069.)

Fisher, G. L., C. E. Chrisp, and W. E. Jennings. 1978. Physical and Chemical Properties of Mutagens in Coal Fly Ash. 12th Annual Conference on Trace Substance in Environmental Health, Columbia, Missouri.

Fisher, G. L., C. E. Chrisp, and O.G. Raabe. 1979. Physical Factors Affecting the Mutagenicity of Fly Ash from a Coal-Fired Power Plant. Science, 204:879.

Floyd, J.R. 1979. Quality Assurance Audit Techniques for Validating Data from Continuous Emission Stack Monitoring (CEM) Systems. 72nd Annual Meeting of the Air Pollution Control Association, Cincinnati, Ohio.

Gasner, L.L. 1977. Enhancement of Sorbent Utilization By the Use of Additives. Proceedings of the Fluidized-Bed Combustion Technology Exchange Workshop, McLean, Virginia, Conf-770447- P-2, Volume 2. U.S. Energy Research and Development Administration.

GCA/Technology Division. 1978. Test Plan for Comprehensive Analysis of Emissions from the Babcock & Wilcox Fluidized-Bed Combustion Unit. GCA Corporation, Bedford, Massachusetts.

Glenn, R.D., and E.B. Robison. 1970. Characterization of Emissions from Fluidized-Bed Combustion of Coal and Control of Sulfur Emission with Limestone. Proceedings of the Second International Conference on Fluidized Bed Combustion, College Corner, Ohio. U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.

Greenwood, D.R., G.L. Kingsbury, and J.G. Cleland. 1979. A Handbook of Key Federal Regulations and Criteria for Multimedia Environmental Control. Research Triangle Institute, Research Triangle Park, North Carolina.

Hansen, Lee D., L. Whiting, D.J. Eatough, T.E. Jenson, and R.M. Izatt. 1976. Determination of Sulfur (IV) and Sulfate in Aerosols by Thermometric Methods. Analytical Chemistry, 48(4):634-638.

Harris, J.C., M.J. Hayes, P.L. Levins, and D.B. Lindsay. 1979. Procedures for Level 2 Sampling and Analysis of Organic Materials. Arthur D. Little Inc., Cambridge, Massachusetts. (EPA-600/7-79-033.)

Harris, J.C., and P.L. Levins. 1978. Interim Procedures for Level 2 Sampling and Analysis of Organic Materials. EPA-600/7-78-016, U.S. Environmental Protection Agency, Industrial Environmental Research Laboratory, Research Triangle Park, North Carolina.

Henschel, D.B. 1977. Environmental Emissions from Coal-Fired Industrial Fluid Bed Boilers. Conference on Engineering Fluidized-Bed Combustion Systems for Industrial Use, Columbus, Ohio.

1979. The EPA R&D Program to Assess the Solid Residue From the Fluidized-Bed Combustion Process. Workshop on Solid Waste Research and Development Needs for Emerging Coal Technologies, San Diego, California.

Herrmann, R., U. Bolz, W. Symader and H. Rump. 1979. Interpretation and Prediction of Spatial Variation in Trace Metals in Small Rivers by Cononical and Discriminant Analysis. Proceedings of the Third International Symposium in Hydrology, Colorado State University, Fort Collins, Colorado.

Horio, M., S. Mori, and I. Muchi. 1977. A Model Study for the Development of Low NO_x Fluidized-Bed Coal Combustors. Proceedings of the Fifth Conference on Fluidized Bed Combustion, Volume 2. The Mitre Corporation, Washington, DC.

Hoy, H.R., and A.G. Roberts. 1977. Further Experiments on the Pilot Scale Pressurized Combustor at Leatherhead, England. Proceedings of the Fluidized Bed Combustion Technology Exchange Workshop, McLean, Virginia, Conf-770447-P-2, Volume 2. U.S. Energy Research and Development Administration.

Ingraham, T.R., and E.M. Zechel. 1979. Selection of Candidate Substances for Control in an Environmental Regulation Agency. Journal of the Air Pollution Control Association, 29:38-42.

International Joint Commission (IJC). 1978. Great Lakes Water Quality Agreement. Great Lakes Regional Office, Windsor, Ontario.

Jacobs, F., and G.C. Grant. 1978. Guidelines for Zooplankton Sampling in Quantitative Baseline and Monitoring Programs. Virginia Institute of Marine Science, Gloucester Point, Virginia. (EPA-600/3-78-026.)

Jarry, R.L., L.J. Anastasia, E.L. Carls, A.A. Jonke, and G.J. Vogel. 1970. Comparative Emissions of Pollutants During Combustion of Natural Gas and Coal in Fluidized Beds. Proceedings of the Second International Conference on Fluidized Bed Combustion, College Corner, Ohio. U.S Environmental Protection Agency, Research Triangle Park, North Carolina.

Jones, C.J. 1978. The Ranking of Hazardous Materials by Means of Hazard Indices. Journal of Hazardous Materials, 2:363- 389.

Kaakinen, J.W., R.M. Jorden, M.H. Lawasani, and R.E. West. 1975. Trace Element Behavior in Coal-Fired Power Plant. Environmental Science and Technology, 9(9): 862.

Keairns, D.L., D.H. Archer, J.R. Hamm, S.A. Jansson, B.W. Lancaster, E.P. O'Neill, C.H. Peterson, C.C. Sun, E.F. Sverdrup, E.J. Vidt, and W.C. Jang. 1975. Fluidized Bed Combustion Process Evaluation: Phase II - Pressurized Fluidized Bed Coal Combustion Development. EPA-650/2-75-027c, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.

Keith, L.H., and W.A. Telliard. 1979. Priority Pollutants I - A Perspective View. Environmental Science and Technology, 13(4):416-423.

Kenson, R.E., and Bartlett, P.T. 1976. Technical Manual for the Measurement of Fugitive Emissions: Roof Monitor Sampling Method for Industrial Fugitive Emissions. U.S. Environmental Protection Agency, Office of Research and Development, Washington, DC.

Kingsbury, G.L., and R.C. Sims. 1978. Preview of the MEG's Supplement. RTI/1430/27-01S, Research Triangle Institute, Research Triangle Park, North Carolina.

Kingsbury, G.L., and J.B. White. 1979. Multimedia Environmental Goals. RTI/1710/04-01S, Research Triangle Institute, Research Triangle Park, North Carolina.

Klein, D.H., A.W. Andren, J.A. Carter, J.F. Emery, C. Feldman, W. Fulkerson, W.S. Lyon, W.C. Ogle, Y. Talmi, R.I. Van Hook, and N. Bolton. 1975. Pathways of Thirty-Seven Trace Elements Through Coal-Fired Power Plant. Environmental Science and Technology, 9(10):973.

Koch, R.C., W.G. Biggs, P.H. Hwang, L. Leichter, K.E. Pickering, E.R. Sawdey, and J.L. Swift. 1977. Power Plant Stack Plumes in Complex Terrain, An Appraisal of Current Research. EPA-600/7-77-020, U.S. Environmental Protection Agency, Environmental Sciences Research Laboratory, Research Triangle Park, North Carolina.

Kolnsberg, H. J. 1976. Technical Manual for Measurement of Fugitive Emissions: Upwind/Downwind Sampling Method for Industrial Emissions. EPA 600/2-76/089a, U.S. Environmental Protection Agency, Office of Research and Development, Washington, DC.

Kolnsberg, H. J., P. W. Kalika, R. E. Kenson, and W. A. Marrone. 1976. Technical Manual for Measurement of

Fugitive Emissions: Quasi-Stack Sampling Method for Industrial Fugitive Emissions. EPA-600/2-76-089c, U.S. Environmental Protection Agency, Office of Research and Development, Washington, DC.

Kolnsberg, H. J., and R. L. Severance. 1979. Development of a Fugitive Assessment Sampling Train for Particulate and Organic Fugitive Emissions. 72nd Annual Meeting of the Air Pollution Control Association, Cincinnati, Ohio.

Landwehr, J.M. 1974. Water Quality Indices - Construction and Analysis. Ph.D. dissertation, University of Michigan, Ann Arbor, Michigan.

Lawrence-Berkeley Laboratory. Environmental Instrumentation Group. 1976. Instrumentation for Environmental Monitoring, Volumes 1 and 2. Lawrence Berkeley Laboratory, University of California, Berkeley.

Lee, M.L., D.K. Later, D.M. Rollins, D.J. Eatough, and L. D. Hansen. 1979. Dimethyl and Monomethyl Sulfate: Presence in Coal Fly Ash and Airborne Particulate Matter. Submitted to Thermal Chemical Institute, Brigham Young University, Provo, Utah.

Lentzen, D.E., D.E. Wagoner, E.D. Estes, and W.F. Gutknecht. 1978. IERL Procedures Manual: Level 1 Environmental Assessment (Second Edition). EPA-600/7-78-201, U.S. Environmental Protection Agency, Industrial Environmental Research Laboratory, Research Triangle Park, North Carolina.

Liu, K.T., G.W. Felton, A.E. Weller, and H. Nack. 1979. Multi- Solid Fluid Bed Combustor - Initial Pilot Plant Results. AIChE 86th National Meeting, Houston, Texas.

Lucke, V.H., and K.R. Murphy. 1977. Environmental Analysis of the General Electric PFB Combined Cycle Power Plant Design. Proceedings of the Fifth International Conference on Fluidized Bed Combustion, Volume 2. The Mitre Corporation, Washington, DC.

Ludwig, C.B., and M. Griggs. 1976. Application of Remote Techniques in Stationary Source Air Emission Monitoring. EPA 340/1-76-005, U.S. Environmental Protection Agency, 2ffice of Enforcement, Washington, DC.

Ludwig, F.L., J.H. Kealoha, and E. Shelar. 1977. Selecting Sites for Monitoring Total Suspended Particulates. Research Institute, Menlo Park, California. EPA-450/3-/7-018, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.

Ludwig, F.L., and E. Shelar. 1978. Site Selection for the Monitoring of Photochemical Air Pollutants. EPA-450/3-78- 013, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.

Lyons, W.A. 1977. Mesoscale Air Pollution Transport in Southeast Wisconsin. EPA-600/4-77-010, U.S. Environmental Protection Agency, Environmental Monitoring Series, Research Triangle Park, North Carolina.

McKenzie, E.C. 1978. Burning Coal in Fluidized Beds. Chemical Engineering, 85(18): 116.

Merryman, E.L., A. Levy, G.W. Felton, K.T. Liu, J.M. Allen, and H. Nack.

1977. Method for Analyzing Emissions from Atmospheric Fluidized-Bed Combustor. EPA-6007-77-034, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.

1978. Method for Analyzing Emissions from Atmospheric Fluidized-Bed Combustor. In Compilation of Level 1 Environmental Assessment Data, eds. N.H. Gaskins and F.W. Sexton. EPA-600/2-78-211, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.

Millan, M.M., and R.M. Hoff. 1976. The COSPEC Remote Sensor, II-Electronic Set-up Procedures. ARQT-6-76, Environment Canada, Atmospheric Environment Service, Downsview, Ontario, Canada.

Mills, M.T., and F.A. Record. 1975. Comprehensive Analysis of Time-Concentration Relationships and Validation of a Single-Source Dispersion Model. EPA-450/3-75-083, U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina.

Mills, M.T., and R.W. Stern. 1975. Model Validation and Time- Concentration Analysis of Three Power Plants. EPA-450/3-76- 002, U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina.

Mitchell, R.E. 1976. Nitrogen Oxide Formation from Chemically- Bound Nitrogen During the Combustion of Fossil Fuels. SAND 76--8227, Sandia Laboratories, Livermore, California.

Moffat, A.J., and M. M. Millan. 1969. The Applications of Optical Correlation Techniques to the Remote Sensing of

SO_2 Plumes Using Sky Light. Symposium on Advances in Instrumentation for Air Pollution Control Administration of the Department of HEW, Cincinnati, Ohio.

Morgan, G. B. 1978. Energy Resource Development: the Monitoring Components. Environmental Science and Technology, 12(1):34-43.

Murthy, K.S., J.M. Allen, D.A. Sharp, and K.M. Duke. 1977. Multimedia Pollutant Emissions Data for Fluidized-Bed Combustion of Coal. Proceedings of the Fifth International Conference on Fluidized Bed Combustion, Volumes 1 and 2. The Mitre Corporation, Washington, DC.

Murthy, K.S., and D.B. Henschel. 1978. Environmental Assessment of Fluidized-Bed Combustion: Status and Results. AIChE 71st Annual Meeting, Miami Beach, Florida.

National Academy of Engineering. 1973. Water Quality Criteria, 1972. U.S. Environmental Protection Agency, Washington, DC.

National Academy of Science. 1972. Particulate Polycyclic Organic Matter. National Academy of Sciences, Washington, DC.

National Institute for Occupational Safety and Health.

1974. NIOSH Manual of Analytical Methods. NIOSH 75-121, U.S. Government Printing Office, Washington, DC.

1976. Registry of Toxic Effects of Chemical Substances. Department of Health, Education, and Welfare Publication, U.S. Government Printing Office, Washington, DC.

National Research Council. 1977. Environmental Monitoring. National Academy of Sciences, Washington, DC.

Newby, R.A., and D.L. Keairns. 1977. Initial Assessment of Alternative SO_2 Sorbents for Fluidized Bed Combustion Power Plants. Proceedings of the Fifth International Conference on Fluidized Bed Combustion, Volume 2. The Mitre Corporation, Washington, DC.

Newby, R.A., N.H. Ulerich, D.M. Bachovchin, C.H. Peterson, N.D. Rohatgi, E.J. Vidt, W.G. Vaux, and D.L. Keairns. 1979. In The Babcock & Wilcox Company, Fluidized Bed Combustion Development Facility and Commercial Utility

AFBC Design Assessment. Technical Progress Report No. 8, Electric Power Research Institute, Palo Alto, California.

Newby, R.A., N.H. Ulerich, E.P. O'Neill, D.F. Ciliberti, and D.L. Keairns. 1978. Effect of SO_2 Emission Requirements on Fluidized-Bed Combustion Systems: Preliminary Technical/ Economical Assessment. EPA-600/7-78-163, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.

Nuclear Regulatory Commission. 1972. Regulatory Guides, Safety Guide 23, On-Site Meteorological Programs. U.S. Nuclear Regulatory Commission, Washington, DC.

NUS Corporation. 1970. Design of Water Quality Surveillance Systems, Phase I Systems Analysis Framework. Federal Water Quality Administration, Washington, DC.

Ott, W.R., 1978. Water Quality Indices: A Survey of Indices Used in the United States. EPA 600/4-78-005, U.S. Environmental Protection Agency, Office of Monitoring and Technical Support.

Pasquill, F. 1974. Atmospheric Diffusion. New York: Halstead Press.

Patterson, W.C., and R. Griffin. 1978. Fluidized-Bed Energy Technology Coming To a Boil. New York: Inform, Inc.

Peeler, J.W. 1979. Continuous Opacity and Particulate Emissions Monitoring in the Federal Republic of Germany: Selected Papers from Current Literature. Entropy Environmentalists, Inc., Research Triangle Park, North Carolina.

Peltier, W. 1978. Methods for Measuring the Acute Toxicity of Effluents to Aquatic Organisms. EPA 600/4-78-012, U.S. Environmental Protection Agency, Surveillance and Analysis Division, Athens, Georgia.

Pereira, F.J., J.M. Beer, B.M. Gibbs, and A.B. Hedley. 1976. NO_x Emissions from Fluidized Bed Coal Combustors. 15th International Symposium on Combustion, Pittsburgh, Pennsylvania.

Petrie, T.W., and G.L. Kingsbury. 1978. Ranking Environmental Impact of Trace Elements in Coal by Use of Multimedia Environmental Goals. RTI/1603/23/01S, Research Triangle Institute, Research Triangle Park, North Carolina.

Pielou, E.C. 1966. Shannon's Formula as a Measure of Specific Diversity, Its Use and Misuse. American Naturalist, 100: 463-465.

Pillai, K.K., and A.G. Roberts. 1977. Emission Characteristics of a Pressurized Fluidized Bed Coal Combustor. Draft. U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.

Piperno, E. 1975. Trace Element Emissions: Aspects of Environmental Toxicology. In Trace Elements in Fuel, ed. S.P. Babu. Advances in Chemistry, Series 141, American Chemical Society, Washington, DC.

Price, J., J. Wiersema, and J. Hartfield. 1979. New Source Review for Acceptability of Public Exposure to Chemical Emissions. 72nd Annual Meeting of the Air Pollution Control Association, Cincinnati, Ohio.

Reznik, R.B., E.C. Eimutis, J.L. Delaney, S.R. Archer, J.C. Ochsner, W.R. McCurley, and T.W. Hughes. 1978. Source Assessment: Prioritization of Stationary Water Pollution Sources. EPA-600/2-78-004q, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.

Robertson, D.E., and R. Carpenter. 1974. Neutron Activation Techniques for the Measurement of Trace Metals in Environmental Samples. Technical Information Center, U.S. Atomic Energy Commission, Oak Ridge, Tennessee.

Ruch, R.R., H.J. Gluskoter, and N.F. Shimp. 1974. Occurrence and Distribution of Potentially Volatile Trace Elements in Coal. EPA-650/2-74-054, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.

Rupp, E.M., D.C. Parzyck, P.J. Walsh, R.S. Booth, R.J. Raridon, and B.L. Whitfield. 1978. Composite Hazard Index for Assessing Limiting Exposures to Environmental Pollutants: Application Through a Case Study. Environmental Science and Technology, 12(7):802-806.

Ryan, L.E., R.G. Beimer, and R.F. Maddalone. 1979. Level 2 Chemical Analysis of Fluidized-Bed Combustor Samples. EPA- 600/7-79-063b, U.S. Environmental Protection Agency, Office of Energy, Minerals and Industry, Research Triangle Park, North Carolina.

Sanders, T.G. 1979. Design of Water Quality Monitoring Systems. Colorado State University, Boulder, Colorado.

Schalit, L.M., and K.J. Wolfe. 1978. SAM/1A: A Rapid Screening Method for Environmental Assessment of Fossil Energy Process Effluents. EPA-600/7-78-015, U.S. Environmental Protection Agency, Office of Research and Development.

Schultz, H., E.A. Hattman, and W.B. Booher. 1975. The Fate of Some Trace Elements During Coal Pretreatment and Combustion. In Trace Elements in Fuel, ed. S.P. Babu. Advances in Chemistry, Series 141, American Chemical Society, Washington, D.C.

Scott, R.D. 1969. The Macro-Invertebrate Biotic Index - A Water Quality Measurement and Natural Continuous Stream Monitor for the Miami River Basin. The Miami Conservancy District, Dayton, Ohio.

Slawson, G.C. Jr., ed. 1979. Groundwater Quality Monitoring of Western Oil Shale Development: Identification and Priority Ranking of Potential Pollution Sources. EPA-600/7-79023, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.

Smith, F. 1978. Level 1 Quality Assurance. Research Triangle Institute, Research Triangle Park, North Carolina. (EPA- 600/7-78-151.)

Sperling, R.B. 1975. Evaluation of the Correlation Spectrometer as an Area SO_2Monitor. PB-249.113, National Technical Information Service.

Sperling, R.B., M.A. Peache, and W.M. Vaughan. 1979. Accuracy of Remotely Sensed SO_2 Mass Emission Rates. EPA-600/2-79- 094, U.S. Environmental Protection Agency, Emissions Measurement and Characterization Division, Office of Research and Development, Research Triangle Park, North Carolina.

Steele, T.D., and T.R. Dyar. 1974. Harmonic Analysis of Water Temperatures of Georgia Streams. Transactions of the American Geophysical Union, 55(12):1114.

Stevens, R.K., and T.J. Dzubay.
1978a. Dichotomous Sampler - A Practical Approach to Aerosol Fractionation and Collection. EPA-600/2- 78-112, U.S. Environmental Protection Agency, Industrial Environmental Research Laboratory, Research Triangle Park, North Carolina.

1979b. Sampling and Analysis of Atmospheric Sulfates and Related Species. Atmospheric Environment, 55-68.

Stone, R., and R. Kahle. 1977. Environmental Assessment of Solid Residues from Fluidized-Bed Fuel Processing. U.S. Environmental Protection Agency, Industrial Environmental Research Laboratory, Research Triangle Park, North Carolina.

Stoner, I.D. 1976. Water Quality Indices for Specific Water Uses. U.S. Geological Survey, Oklahoma City, Oklahoma.

Sugarek, R.L., and T.G. Sipes. 1978. Controlling Sulfur Dioxide Emission from Coal-Fired Steam-Electric Generators: Water Pollution Impact, Volume 2, Technical Discussion. U.S. Environmental Protection Agency, Industrial Environmental Research Laboratory, Research Triangle Park, North Carolina.

Sun, C.C., and J.T. McAdams. 1979. Assessment of RCRA/EP Test Results on FBC Residue. Westinghouse R&D Center, Pittsburgh, Pennsylvania.

Suprenant, N., R. Hall, S. Slater, T. Susa, M. Sussman, and C. Young. 1976. Preliminary Emissions Assessment of Conventional Stationary Combustion Systems, Volume 2 - Final Report. GCA/Technology Division, Bedford, Massachusetts. Prepared for U.S. Environmental Protection Agency. (Publication Number EPA-600/2-76-046b.)

Swartz, R.C. 1978. Techniques for Sampling and Analyzing the Marine Macrobenthos. Corvallis Environmental Research Laboratory, Newport, Oregon. (EPA-600/3-78-030.)

Swift, W.M., S.H.D. Lee, J.C. Montagna, G.W. Smith, I. Johnson, G.J. Vogel, and A.A. Jonke. 1977. Plans and Studies on Flue Gas Cleaning and Particulate Monitoring in PFBC. Proceedings of the Fifth International Conference on Fluidized Bed Combustion, Volume 2. The Mitre Corporation, Washington, DC.

Symader, W., and W. Thomas. 1978. Interpretation of Average Heavy Metal Pollution in Flowing Waters and Sediment by Means of Hierarchical Grouping Analysis Using Two Different Error Indices. Cantena, 5(2):133-144.

Todd, D.K., R.M. Tinlin, K.D. Schmidt, and L.G. Everett. 1976. Monitoring Groundwater Quality: Monitoring

Methodology. EPA-600/4-76-026, U.S. Environmental Protection Agency, Office of Research and Development.

TSCA Interagency Testing Committee (CEQ). 1977. Initial Report of the TSCA Interagency Testing Committee to the Administrator, Environmental Protection Agency. Federal Register, Vol. 42, No. 197.

Turner, B. 1974. Workbook of Atmospheric Dispersion Estimates. Publication Number AP-27, U.S. Environmental Protection Agency, Office of Air Programs.

U.S. Environmental Protection Agency.

1973. Handbook for Monitoring Industrial Wastewater. U.S. Environmental Protection Agency, Technology Transfer, Washington, DC.

1976a. Guidelines for Evaluating Supplementary Control Systems. EPA-450/2-76-003, U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina.

1976b. A Technique for Supplementary Control System Reliability Analysis and Upgrading. EPA-450/2-76- 015, U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina.

1976c. Quality Criteria for Water. U.S. Environmental Protection Agency, Office of Water and Hazardous Materials, Washington, DC.

1977a. Proposed National Interim Secondary Drinking Water Regulations. Environment Reporter - Current Developments, 7(49):1884-1887.

1977b. Sampling and Analysis Procedures for Screening of Industrial Effluents for Priority Pollutants. U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio.

1978a. Ambient Monitoring Guidelines for Prevention of Significant Deterioration (PSD). EPA-450/2-78-019, U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina.

1978b. Guideline on Air Quality Models. EPA-450/2-78-027, U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina.

1978c. National Interim Primary Drinking Water Regulations. Code of Federal Regulations, Title 40, Part 141.11.

1979a. Methods for Chemical Analysis of Water and Wastes. EPA-600/4-79-020, U.S. Environmental protection Agency, Technology Transfer, Washington, DC.

1979b. Ohio: Approval and Promulgation of Implementation Plans - Proposed Rule. Federal Register, Vol. 44, No. 114:33711-33712.

1979c. Regulations on National Primary and Secondary Ambient Air Quality Standards. Federal Register, Vol. 44, No. 28: 8221.

1979d. Water Quality Criteria - Request for Comments. Federal Register, Vol. 44, No. 52: 15926-12981.

U. S. Geological Survey. 1976. Selected Methods of the U. S. Geological Survey for Analysis of Wastewaters. Report No. 76-177, U. S. Geological Survey, Reston, Virginia.

Veldman, D.J. 1967. FORTRAN Programming for the Behavorial Sciences. New York: Holt, Rinehart, and Winston.

Walsh, P. J., G. G. Killough, and P. S. Rohwer. 1978. Composite Hazard Index for Assessing Limiting Exposures to Environmental Pollutants: Formulation and Derivation. Environmental Science and Technology, 12:799-807.

Ward, R.C. 1979. Regulatory Water Quality Monitoring: A Systems Perspective. Water Resources Bulletin, 15(2):369- 380.

Weber, C. I. 1973. Biological Field and Laboratory Methods for Measuring the Quality of Surface Waters and Effluents. EPA-670/4-73-001, U.S. Environmental Protection Agency, Washington, DC.

Weber, E. 1970. Determination of the Life Time of SO_2 by Simultaneous CO_2 and SO_2 Monitoring. Second International Clean Air Congress of the International Union of Air Pollution Prevention Associations, Washington DC.

Weber, J.B. 1977. The Pesticide Scorecard. Environmental Science and Technology, 11:756-761.

White, H.J. 1968. Characteristics of Particulate Matter. Industrial Water and Wastes Magazine, 48-56.

Wilhm, J.L.

1967. Comparison of Some Diversity Indices Applied to Populations of Benthic Macroinvertebrates in a Stream Receiving Organic Wastes. Journal of the Water Pollution Control Federation, 39(10):1673-1683.

1970. Range of Diversity Index in Benthic Macroinvertebrate Populations. Journal of the Water Pollution Control Federation, 42(5):R221-224.

Yang, R.T., M.S. Shen, and M. Steinberg. 1978. Fluidized-Bed Combustion of Coal with Lime Additives: Catalytic Sulfation of Lime with Iron Compounds and Coal Ash. Proceedings of the Fifth International Conference on Fluidized Bed Combustion, Volume 2. The Mitre Corporation, Washington, DC.

Yaverbaum, L. 1977. Fluidized Bed Combustion of Coal and Waste Materials. Noyes Data Corporation, Park Ridge, New Jersey.

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APPENDIX A

GUIDELINES FOR DEVELOPING A QUALITY ASSURANCE PROGRAM FOR AMBIENT MONITORING ASSOCIATED WITH ENERGY TECHNOLOGIES

INTRODUCTION

New types of energy technologies such as FBC of coal, in-situ oil shale conversion, and coal gasification or liquefaction require different monitoring strategies. These strategies, which are employed to prevent adverse effects on the environment, may include ambient source-oriented monitoring to determine the environmental concentration and fate of potentially dangerous byproducts (Dalton·Dalton·Newport, 1978). The data derived from ambient source-oriented monitoring may be used by the EPA to establish standards and regulations, provide dose estimates of toxic materials and possible health effects, and support enforcement activities. For these uses, the data generated must be accurate, precise, and legally and scientifically defensible.

Much environmental monitoring information is currently available from a wide range of federal, state, and local agencies, corporations, individuals, and special interest groups. However, in some cases, data for which considerable time, money and effort had been expended have been found virtually useless because of the lack of validity, accuracy or completeness. Many of these inadequacies are directly attributable to the lack of a defined and implementable quality assurance program. To correct this problem, the EPA now requires a quality assurance program as an integral part of any research or monitoring activity.

Quality assurance is a system for integrating the quality planning, quality assessment and quality improvement efforts of an organization. The system is designed to assure the output of a quality product--in this case, data that are valid, accurate, precise, complete, and comparable to data generated on other projects or collected at different times on the same subject.

Quality assurance includes both the operational activities associated with production of a quality product (quality control) and the administrative activities required to support quality control and promote implementation of standards of quality. Quality control includes routine checks of normal operating procedures such as periodic calibration of instruments, performing duplicate analyses, analysis of split samples and spiked samples, examination of data for validation, and maintenance of equipment. Administrative activities include designing the quality assurance program, establishing performance standards, and periodically verifying performance of quality control activities.

The latter typically includes administrative evaluation of quality control and associated activities and an independent audit of the entire quality assurance program. The independent audit is often performed by a representative of a regulatory agency. Although the independent auditor is not a member of the organization conducting the monitoring, the auditing activity is considered part of the quality assurance system.

OBJECTIVES

The objectives of a quality assurance program are to: (Smith and Wagoner, 1974)

- Minimize systematic and random variability in the measurement and data collection processes.
- Provide for prompt detection and correction of conditions that would contribute to the collection of poor quality data.
- Collect and supply information to describe the quality of the data.
- Evaluate the overall adequacy of the data-gathering process as it affects data quality.

To accomplish these objectives, a quality assurance program must have several components. These required components are divided into two general groups, each of which includes several elements. The quality assurance activities associated with each element may involve both administrative and operational activities.

The elements are:

- Organization
  - Quality assurance plan
  - Quality assurance coordination
  - Training of personnel
  - Procurement and facilities development
  - Documentation control
  - Auditing

- Documentation of Operations and Procedures
    - Sample site selection
    - Sample collection
    - Analytical methods
    - Data reporting
    - Data validation
    - Test and instrument calibration
    - Preventive maintenance

ORGANIZATION

Quality Assurance Plan

To produce a quality assurance program that satisfies the needs of data users, management, and the operators, a plan should be provided by management. A quality assurance plan outlines the quality objectives of the organization and the lines of responsibility and manner of interactions between management and operations personnel. The activities required to achieve the quality objectives of the organization should be listed. A quality assurance coordinator should be designated and authorized to implement the quality assurance plan. Management must visibly support the program at all levels of the organization, and commit the resources necessary to implement the quality assurance activities.

The quality assurance plan must:

- Outline the administrative structure of the laboratory, including an organizational chart.
- Define the accountability of all personnel whose actions have an impact upon data quality.
- Define of the duties of the quality assurance coordinator with respect to production of quality data, including clear lines of authority.
- Outline the plan to train personnel who produce the data.
- Describe how and by whom equipment will be procured.
- Establish facilities suitable for data gathering and analysis activities.

Quality Assurance Coordination

The overall responsibility for coordination and implementation should be assigned to one person, the quality assurance coordinator. He will serve as the advisor to management in developing the quality assurance program and as liaison between operations supervisors and management for all actions having a bearing on the quality of the data produced by the organization. In no case should the coordinator be subordinate to supervisors having direct control over sampling and analytical operations; rather, the supervisors and analysts should actively assist the coordinator's efforts in implementing the program on a daily basis. Figure A-1 illustrates the activities associated with a quality assurance program and the possible interactions of the coordinator with the analytical and supervisory personnel.

A major function of the quality assurance coordinator is to provide evaluation reports to all levels of the organization. The reports may include basic statistics describing the validity of the data, information on trends, corrective actions which are required or were taken, and evaluation of performance of the laboratory. The frequency of the reports and their content depend on the organizational level to which they are being directed. Reports to a laboratory supervisor may be on a weekly basis, and include the specific information required to identify any problems and suggest corrective action. Reports to a manager having responsibility for production as well as monitoring may be necessary only semi-annually and include information on trends and evaluation of performance.

Another function of the quality assurance coordinator is to assure that standards and quality control samples are properly obtained or prepared and analyzed in a manner representative of normal operating conditions. A third function is to insert controls to assure that the data-gathering activities meet the stated requirements for accuracy and precision.

The quality assurance coordinator for a facility conducting environmental monitoring maintains contact with personnel of state and federal regulatory agencies to assure that changes in requirements and regulations are implemented on schedule. The coordinator may also discuss laboratory evaluation with the regulatory agencies and coordinate intraand inter-laboratory auditing of performance of the laboratory.

Training of Personnel

The knowledge of the operators and the techniques that they use to perform their tasks will define or control the ultimate quality of the data. Therefore, training of the operators is important. Training goals serve to assure that the output is accurate and precise, that each operator performs a given task in the same manner, that operator bias is reduced and controlled, and that the operator is a manager of

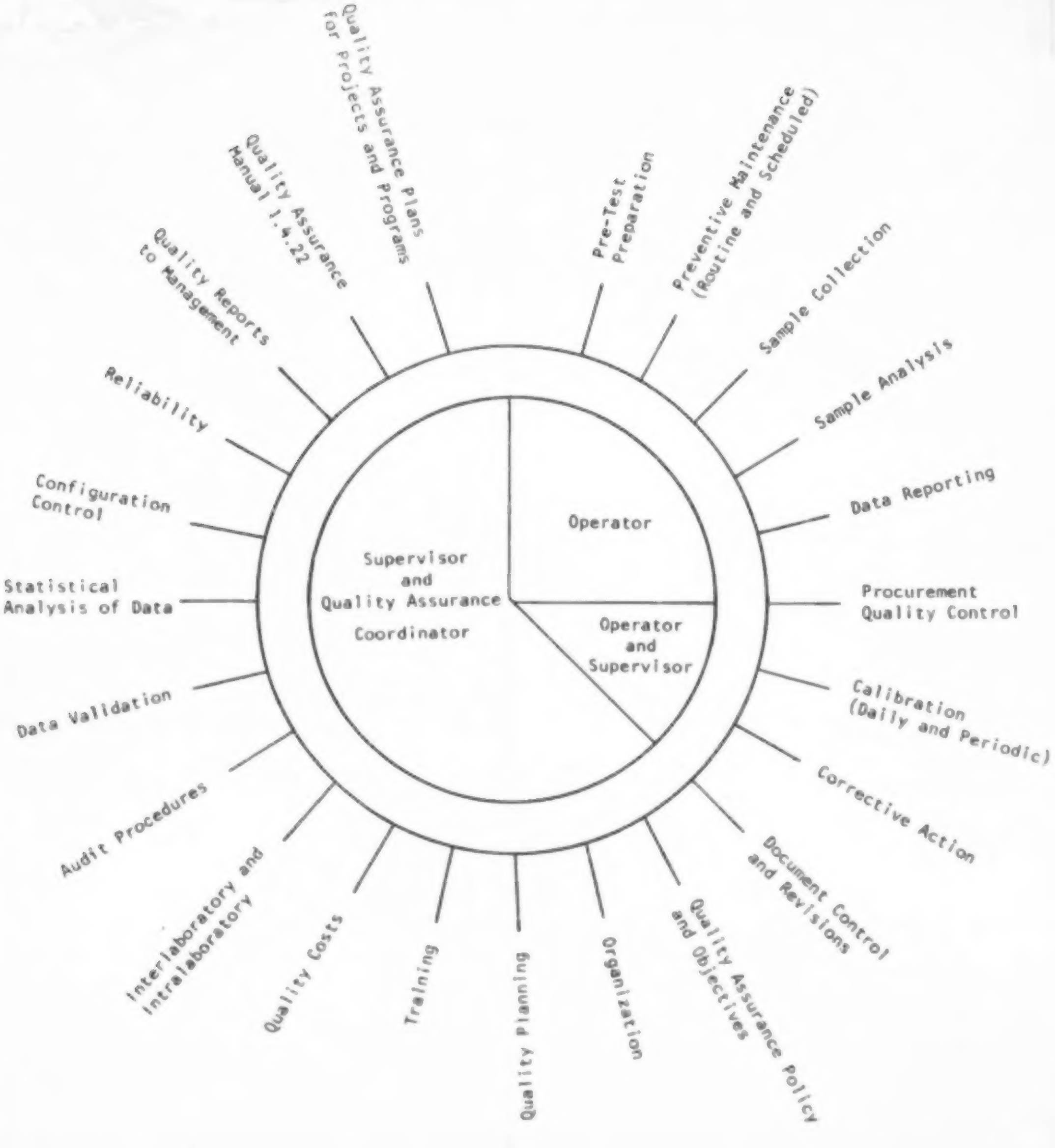

Quality Assurance Plans for Projects and Programs
Quality Assurance Manual 1.4.22
Quality Reports to Management
Reliability
Configuration Control
Statistical Analysis of Data
Data Validation
Audit Procedures
Interlaboratory and Intralaboratory
Quality Costs
Training
Quality Planning
Organization
Quality Assurance Policy and Objectives
Document Control and Revisions
Corrective Action
Calibration (Daily and Periodic)
Procurement Quality Control
Data Reporting
Sample Analysis
Sample Collection
Preventive Maintenance (Routine and Scheduled)
Pre-Test Preparation
Operator
Operator and Supervisor
Supervisor and Quality Assurance Coordinator

Figure A-1. Quality assurance elements and responsibilities (The Quality Assurance Wheel).

(EPA, 1976)

the measurement system rather than a part of it. Controlling operator bias so that it is constant for all operators allows different operators to obtain the same information for a given sample and measurement system.

To meet training goals, the following elements are required:

- Develop a programmed training procedure that includes not only the mechanics of the procedures but also the performance standards.
- Define the reasons for and benefits of standards of quality; explain why high quality is essential and what constitutes acceptable quality.
- Determine the proficiency of the operator and acceptability of the operator's output through the use of control samples and quality standards.
- Verify the accuracy of the operator's output and correct defects.

Following the steps outlined above will provide necessary direction to the personnel, accentuate the need for quality control as an integral part of the data collection process, and provide a basis for routine quality control and systematic checks on the output of the operators. The mechanics of the training process might include: 1) observing the procedure performed by an experienced analyst, 2) reviewing the theoretical and operational steps involved in a procedure, and 3) performing "hands-on" analysis under direct supervision, followed by independent operation. Accuracy of the data obtained in the last phase should be immediately verified and the operator's understanding of the theory and techniques involved evaluated.

The training program should include both old and new personnel, with periodic assessments of additional training needs. The program might include formal classroom training as well as the on-the-job training outlined above. The formal training might involve general theory and applications taught at colleges and technical schools, or more specific training such as short courses and workshops offered by the EPA and other groups.

The training courses offered by the EPA cover a wide spectrum of techniques including sampling, analysis, data reduction, and statistics applicable for both air and water monitoring. Information on the courses available can be obtained from:

National Training and Operational Technology Center
U.S. Environmental Protection Agency
26 West St. Clair
Cincinnati, Ohio 45268

Registrar, Air Pollution Training Institute
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Procurement and Facilities Development

Procurement of equipment and materials and development of a suitable facility are important functions, and will involve management, the quality assurance coordinator, and the operations supervisors. This phase of the program will assure that the operational tasks can be performed in an efficient, effective manner which is consistent with the quality goals of the organization. The prime criterion for acquisition of equipment is that it must be suitable to perform the intended tasks. In general, the equipment needs are dictated by the parameters being measured; the methods used to measure the parameters; and the sensitivity, reliability, and accuracy required.

The quality assurance plan should: 1) describe the criteria to be used in selection and acceptance of equipment and material used in the monitoring program, 2) define responsibility for ordering equipment, maintaining the equipment inventory, and determining whether the equipment meets the acceptance criteria, and 3) specify the degree of control that the operations supervisors and the quality assurance coordinator have over the selection of equipment. It is the responsibility of the quality assurance coordinator to see that the criteria for equipment acquisition are met and are consistent with the quality goals of the organization.

Documentation Control

Documentation control is the process which describes the route and mechanism for disseminating information through the organization. All procedures for collecting, analyzing, and distributing data and information must be thoroughly documented and readily available. The quality assurance plan should also detail the mechanism for establishing and revising procedures. The details to be covered in the plan concerning revisions or additions to established documents include:

- The lines of responsibility for making the revisions.

- A distribution plan to assure effective implementation of the revisions or additions.

- The mechanism to be used in validating the revisions or additions.

Auditing Procedures

Each monitoring system must be audited to evaluate the quality assurance program and the quality of data produced by the monitoring program. Two types of audits can be performed, performance audits and system audits. Performance audits are quantitative assessments of data quality; system audits are qualitative assessments of data quality.

Performance audits are checks by an independent auditor to evaluate the quality of data produced by the total sampling and analysis system. The following are examples of performance audit procedures commonly used:

- Observation of sampling and transportation techniques and procedures, and use of calibrated meters or reference standards to check the performance of sampling equipment.
- Observation of actual laboratory analytical techniques, and providing standards or reference samples for analysis.
- Observation of data-processing methods, spot checking calculations and data-validation procedures by insertion of a set of dummy data into the processing system, and reviewing the validated data.

Performance audits may be conducted by several levels of personnel. These may include checks of:

- An analyst's output by another analyst or operator
- The output of one or more analysts by a supervisor
- The output of the data production process by the quality assurance coordinator
- The output of the data production process by an independent auditor

The quality assurance plan should incorporate all levels of auditing, and describe the frequency at which the audits are to be performed. In general, the auditor will be working from a checklist to assure that all pertinent factors are considered. Items on the checklist may be simple, e.g., checking a balance with approved weights; or more complicated, e.g., checking continuous air pollutant monitors for each variable which may affect the output. The checklist should identify the critical variables for each measurement or parameter, and the control limits for passing the audit.

A systems audit is an on-site inspection and review of the quality assurance program as it is applied to the total measurement system. The quality assurance plan is the basis for the systems audit. The questions to be answered in the system audit include:

- Is the plan sufficiently detailed, and is it operational?
- Are sample collection and analytical procedures adequately described and available for use by appropriate personnel, and are they being followed?
- Are instrument and test calibration procedures available to appropriate personnel and are they being followed?
- Are calibration results available and do they establish traceability to standards of higher quality (National Bureau of Standards or equivalent)?
- How frequently are control charts and quality control data reviewed?
- Are data quality problems handled quickly and efficiently?
- Does the laboratory adhere to the preventive maintenance schedule outlined in the quality assurance plan?
- Are the results of interlaboratory tests and other quality assurance analyses examined and used for improvement of operations?

A usable system audit checklist and suggested method for grading quality assurance program performance is available (Buchanan, 1976).

An essential part of a quality assurance program for any monitoring activity is periodic performance and system audits. These audits are to be conducted by an organization or agency independent of the organization conducting the monitoring. Under present EPA guidelines, individual states assume the roles of administrator and inspector to assure that laboratories within their jurisdiction are performing adequately. It is therefore likely that a state agency will at least partially fulfill the requirements of an independent auditor. The state agencies often perform the two types of audits simultaneously.

It is recommended that an independent audit of monitoring and quality assurance programs associated with energy production and conversion facilities be performed at least once a year. If the state agency which would be responsible for the audits cannot conduct yearly audits, the organization conducting the monitoring should contract an outside firm approved by the appropriate regulatory agency to conduct the audits.

DOCUMENTATION OF OPERATION AND PROCEDURES

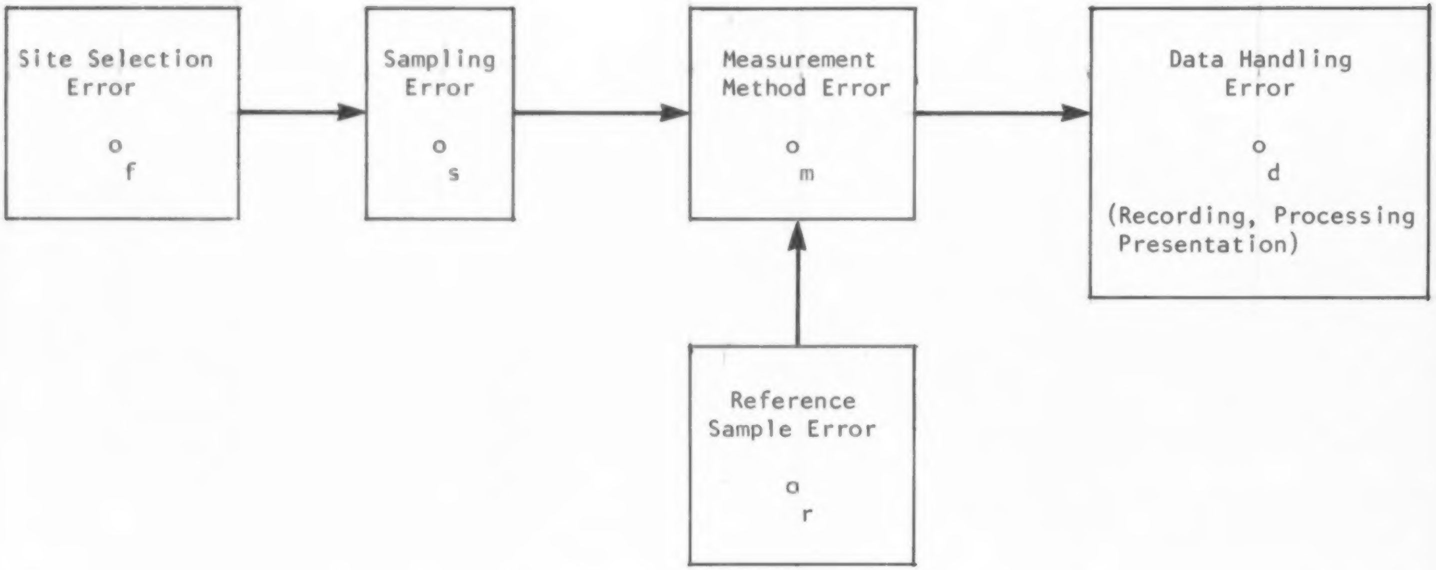
The following discussion reviews the major operational elements of an ambient monitoring program. The major elements of an extractive monitoring system are shown in Figure A-2. Errors in any of the elements can lead to erroneous data. Quality control efforts and methods, e.g., procedures documentation, should serve to eliminate sources of error. Some of the important factors of each element which may affect the quality of the data are discussed. Thorough documentation of sampling, analysis, data processing, maintenance and all other procedures is essential. Many methods and guidelines are available for reference and methods selection. The documentation should describe how various methods are used in the monitoring program.

Sample Site Selection Procedures

Selection of representative sample sites is a major factor in assuring that ambient monitoring data properly reflect the environmental impacts of pollutants from traceable sources. Efficient and cost-effective monitoring requires the selection of the fewest number of sample sites needed to adequately characterize ambient conditions. Determining the number and locations of the sampling sites requires a survey of the affected area. Among the points to be considered in the survey are:

- The parameters to be monitored
- Topography of the area
- Meteorological conditions and variability
- Location and types of emissions
- Location, volume of flow and direction of flow of surface and ground waters
- Population density of the affected area
- Types of downstream water, air and land uses.

To select sample sites and design the monitoring program, it is necessary to obtain detailed information concerning the above criteria. The selection of the number, location and


Site Selection Error
o_f
Sampling Error
o_s
Measurement Method Error
o_m
Data Handling Error
o_d
(Recording, Processing Presentation)
Reference Sample Error
o_r

$$o_t = \sqrt{o_f^2 + o_s^2 + o_m^2 + o_r^2 + o_d^2}$$

Figure A-2. Major components of system errors in an extractive monitoring system. (Total error is the sum of the individual terms.)

(Environmental Science and Technology, 1978) type of sampling stations is a complex problem; each sampling network must be developed individually. In general, simple and homogenous environments require relatively few sample sites, whereas complex and heterogeneous environments require a greater number to adequately characterize ambient conditions.

For ambient surface water monitoring, the number and location of sampling sites may be affected by the number of known and potential discharge points associated with any facility to be monitored. In general, at least one upstream and one downstream site relative to a discharge are necessary. The upstream sample site should be located to represent ambient stream conditions. Selection of downstream sample sites is based on the location of the mixing zone of the effluent stream in the receiving water. In some cases, the downstream site for a source may constitute an upstream site for the next downstream source. Thus, information may be required on the rate of flow, density, and temperatures of both the effluent and the receiving stream. Cross-sectional transect profile analysis should be performed to determine the specific location of sample sites if a source is point or discrete non-point in nature and if grab samples are to be collected.

Groundwater monitoring may be required for in situ processes and other situations in which an aquifer is likely to be contaminated by pollutant-bearing surface runoff. Groundwater should be sampled from monitoring wells designed and drilled for that purpose. However, existing wells are often used with satisfactory results. The location of the wells should be determined based upon a hydrogeologic analysis of the site. This may include drilling test wells and performing standard tests to determine water quality, flow direction, and aquifer characteristics. Details of the tests and determination of groundwater flow characteristics in an aquifer are documented (Walton, 1970; Todd, 1967; Davis and DeWiest, 1966). It is critical to locate water quality monitoring wells on the basis of the hydrologic analysis to assure that the pollutant pathway is being monitored.

The meteorologic conditions of an area affect the dispersion of air pollutants and consequently the location of sampling equipment needed to monitor ambient air quality. The National Weather Service currently obtains meteorological data which may be adequate to support ambient monitoring programs. Additional meteorological data might be required for areas where existing meteorological data are insufficient or unrepresentative of local conditions. The need to collect site-specific data may arise from peculiarities in local emission sources and topographical features such as hills, valleys, trees, lakes, and urban heat islands.

For certain monitoring purposes, the placement of probes or sampling equipment is of prime importance for obtaining the desired data. The Ambient Monitoring Guidelines for Prevention of Significant Deterioration (PSD)(EPA, May 1978a) specifies probe placement criteria in an effort to minimize effects of topographical features and direct sources of pollutants upon measurement of ambient conditions. Table A-1 summarizes the specific probe siting guidelines for the PSD ambient monitoring program.

Two quality assurance steps must be observed with regard to the selection of sampling locations:

- Data records that justify the selection of each sample site should be maintained and open for inspection by appropriate auditing personnel or agencies. The data should include detailed maps and photographs of each sampling site selected.
- Following preliminary and/or final sample site selection, an independent auditor should verify the adequacy of the selected sample locations in satisfying the objectives of the ambient monitoring program. The independent auditor should be a recognized authority in the field of sample site selection, and may be either a private consultant or a reprentative of an appropriate regulatory agency.

Sample Collection Procedures

Generally, each major sampling category (air, surface water or groundwater) will have a separate protocol. The procedures must specify:

- Types of samples collected and the techniques used to collect them
- Numbers of samples to be collected and the frequency of sampling
- Amounts or volumes of samples to be collected and methods of preservation
- Means of sample transfer and storage and holding time requirements
- Methods for permanent identification of samples
- Procedure to assure chain of custody

TABLE A-1. **SUMMARY OF PROBE SITING CRITERIA**
(EPA, May, 1978a)

Pollutant	Height above ground, meters	Distance from supporting structure, meters: Vertical	Distance from supporting structure, meters: Horizontal*	Other spacing criteria
TSP	2 - 15	--	>2	a. >0 meters from trees b. Distance from sampler to obstacle, such as buildings, must be at least twice the height the obstacle protrudes above the sampler c. Unrestricted airflow in 3 of 4 cardinal wind directions d. No furnace or incineration flues should be nearby** e. Spacing from roads varies with height of monitor
SO_2	3 - 15	>1	>1	a. Probe on roof or intermediate height on a building must be <0.8 of the mean height of the building in the neighborhood b. >20 meters from trees c. Distance from sampler to obstacle, such as buildings, must be at least twice the height the obstacle protrudes above the sampler d. Unrestricted airflow in 3 of 4 cardinal wind directions e. No furnace or incineration flues should be nearby**
CO	3 ± 1/2	>1	>1	a. >35 meters from roadway b. Unrestricted air flow in 3 of 4 cardinal wind directions
O_3	3 - 15	>1	>1	a. >0 meters from trees b. Distance from sampler to obstacle, such as buildings, must be at least twice the height the obstacle protrudes above the sampler c. Unrestricted airflow in 3 of 4 cardinal wind directions d. Spacing from roads varies with roadway traffic
NO_2	3 - 15	>1	>1	a. >20 meters from trees b. Distance from sampler to obstacle, such as buildings, must be at least twice the height the obstacle protrudes above the sampler c. Unrestricted airflow in 3 of 4 cardinal wind directions d. Spacing from roads varies with roadway traffic

* When probe is located on rooftop, this separation distance is in reference to walls, parapets, or penthouses located on the roof.

** Distance is dependent on height of furnace or incineration flue, type of waste or fuel burned, and quality of fuel (sulfur and ash content). This is to avoid undue influences from minor pollutant sources.

- Procedures for verification of data from continuous monitoring instruments

The primary purpose of a sample system is to collect representative samples. Grab samples from environmental media generally provide neither average concentration data nor variations in concentration, and should be avoided where possible. Automated sampling or monitoring equipment is usually necessary to quantify variations in environmental quality caused by variations in source effluent quality. In some types of monitoring programs, however, information derived from grab samples may be sufficient to satisfy the program objectives. Samples collected by automated equipment may be collected in relation to time, or in proportion to flow.

The quality assurance points which must be documented include:

- Methods for calibrating the timing and volume control sequences

- The appropriate analytical quality control and quality assurance points if the sampler is also an analyzer

- Variations allowed for the environment in which the sampler is located and methods for controlling them

- The nature, number and frequency of fluid samples to be submitted by the sampling personnel to the laboratory including the responsibility for and methods of preparation of such samples

- Procedures for maintaining all records

- Acceptance criteria for evaluating the results of blind sample analyses, and the variation in sampler operation

The volume of sample to be collected depends on both the parameter being measured, and the measurement technique. For example, measurement of metals by flame atomic absorption may require a liter of sample, whereas flameless methods might require only 20 ml of sample.

The preservation techniques to be used also depend on the nature of the sample and the parameters to be measured. The requirement may range from simple refrigeration to addition of several reagents. For example, phenol samples require the addition of copper sulfate and phosphoric acid and subsequent refrigeration.

The "chain of custody" is a specified regimen of sample identification, handling, and transfer procedures which must be observed if data validity is to be assured. Where it is known that samples are being collected as part of an enforcement action or other legal proceeding in which data and information could be presented in court, rigorous adherence to chain of custody procedures is required. The chain of custody procedures to be employed should be those developed by the National Enforcement Investigation Center (EPA, May 1978b). The main points of the chain of custody procedures are:

- Complete documentation of sample and data possession is required from collection to final utilization. A sample is in your custody if:
  - It is in your physical possession,
  - It is in your view after being in your possession,
  - It was in your possession and you locked it in a secure area.
- The smallest number of people possible should handle the samples in the field, during transfer, and during analysis.
- Each person handling the samples or data is responsible for their care and custody until properly transferred or dispatched.
- Sample identification tags and the chain of custody form must be attached to the sample at the time of collection. The information on the tags should:
  - State sample number, time sample was taken, source of sample, type of sample, preservatives used and analyses required
  - State the name of the sample collector and any witnesses
  - Be filled out in permanent (waterproof) ink
- Blank samples with and without preservatives may be necessary as a check on possible contamination.
- Maintenance of log books is required. The information recorded shall be that which is necessary to establish the validity and chain of custody of the samples and subsequent data. It includes all sample data, field measurements, calibrations performed, and any other pertinent information.
- The chain of custody record shall be signed and dated by each person who handles the sample, indicating the time it came into and left his possession.

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- Deviations from the methods specified in the quality assurance plan must be noted and justified.

It is highly recommended that the NEIC chain of custody procedures be employed for routine sampling and analysis even if it is believed that the data will not be used in a legal proceeding.

Analytical Procedures

All analytical procedures used to measure the concentration of contaminants in an ambient monitoring program shall be thoroughly documented. The quality assurance requirements for documentation include:

- Documentation of analytical method
- Description of methods for recording and maintaining analytical data
- Description of the quality control measures to be observed for each parameter measured

The universe of potential pollutants from the energy technologies lists over 1,000 elements and compounds (Murthy and Henschel, 1978). For some of the major pollutants and those for which standards are in effect, the EPA has published or accepted official methods. For the many other possible pollutants, however, no official method exists, although numerous tentative procedures are available. Some official and accepted methods and sources are listed in the Bibliography at the end of this Appendix.

If an official or tentative EPA method exists to measure the concentration of a parameter, that method shall be used. For those parameters for which no official or tentative method exists, one will have to be developed, and the following information describing its suitability must be available:

- A detailed, step-by-step description of the techniques used for the analysis
- A list describing all specialized or unusual equipment used in the analysis
- The sensitivity of the analysis and the limits of detection for the parameter
- The accuracy and precision which should be obtainable under routine operating conditions
- A description of any interferences and how they would affect the accuracy, precision or sensitivity of the analysis, with particular attention given to the interferences likely to be found in typical samples

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(PREVIOUSLY EIN. EPA FORM 387)
TYPING GUIDE SHEET

- A list of the references used to develop the techniques.

Each laboratory performing analyses is to keep a written account of each method as it is actually performed. Any irregularities or differences in the method used as compared to an official method must be noted and justified to the extent that the accuracy, precision or sensitivity of the test is affected. Criteria for comparison of new or alternate test procedures may be found in Guidelines Establishing Test Procedures for the Analysis of Pollutants (Federal Register, December 1976).

All analytical or experimental data are to be recorded permanently. Bound logbooks are preferred for recording and permanently storing data which is manually produced. Computer storage is often preferred for automated monitoring systems because of the volume of data produced. The data should be recorded in such a fashion that the work performed is clear to anyone wishing to check the results or the manner in which they were obtained. At a minimum, the information in the logbook must include:

- The date the analysis took place
- Complete description or identification of the sample being analyzed
- Parameter being analyzed
- Analytical method used
- Results of analytical standards or calibrations
- Calculations
- Volume of sample used
- Dilutions or concentrations required
- Any difficulties or problems encountered during the analysis and a description of how they were dealt with (If the difficulties would affect the accuracy, precision or recovery of the parameter, the steps performed to assess the degree of difficulty must be described.)
- The results of duplicate, replicate or check samples must be noted

In general, the analytical records must be retained a minimum of three years and must be made available to the agencies or contractors responsible for auditing the results. The quality control measures required during analysis depend to a degree on the method being used to measure pollutant concentrations. For instrumental methods, the instrument should be calibrated with a minimum of three standards. The concentration range of the standards must cover the expected concentration of the parameters being measured. Some instrumental air monitoring methods require daily or weekly zero and span calibrations and quarterly six-point linearity checks.

For instrumental and non-instrumental methods of analysis, determination of precision and accuracy for all parameters is required.

Precision is the reproducibility among replicate observations. The precision may be based on measurement of duplicate samples, or on span checks for instrumental measurement of gaseous air pollutants. The measurement of precision must cover the range of concentrations expected for each parameter, the variety of interferences likely to be encountered, and the different sample types analyzed. The sample types might include contaminated and uncontaminated surface and ground waters, and contaminated and uncontaminated air samples. Precision is stated as the standard deviation of the replicate observations, and must be presented in terms of the concentration of the parameter for each type of sample measured.

Accuracy, the difference between observed values and known or actual values, can be determined by adding known amounts of a contaminant to a sample, and calculating the percentage recovery for that parameter. In some cases, accuracy can be measured by direct analysis of a standard reference material or by analysis of a synthetic sample that contains known amounts of a contaminant in a matrix approximating that of samples. Accuracy should be determined at different levels of pollutant concentrations, and on samples that cover the full range of expected sample types and interferences. Table A-2 summarizes some of the quality control samples available from the EPA.

Round-robin studies, in which many laboratories analyze a particular parameter by a specified method, are often used to determine accuracy and precision of analytical methods. This type of analysis serves two functions: 1) determines which of the methods tested for a given parameter provides the highest degree of accuracy and precision, and 2) determines the accuracy and precision attainable under routine operating conditions for a given method. The accuracy and precision statements from round-robin studies are generally regarded as the standard of performance for an analytical method.

Quality control charts are a method of graphically presenting the precision and accuracy data and comparing them against established limits of precision and accuracy for a given test and set of operating conditions. The control charts can readily identify trends in an analysis and determine when an analysis is out of control. Quality control charts are recommended as the method for recording and interpreting precision and accuracy data generated in monitoring programs associated with energy production and conversion facilities.

TABLE A-2. QUALITY CONTROL SAMPLES AVAILABLE FROM THE EPA ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY, CINCINNATI

Nutrient Analyses - Two Levels
  - Nitrate-N
  - Kjeldahl-N
  - Orthophosphorous
  - Ammonia-N
  - Total Phosphorous

Demand Analyses - Two Levels
  - BOD
  - COD
  - TOC

Mineral Analyses - Two Levels
  - Sodium
  - Potassium
  - Calcium
  - Magnesium
  - Alkalinity/acidity
  - Total Hardness
  - Total Dissolved Solids
  - Specific Conductance
  - Sulfate
  - Chloride
  - Fluoride
  - pH

Mercury Analyses - Three Levels
  - Organic
  - Inorganic

Trace Metals Analyses - Three Levels
  - Aluminum
  - Arsenic
  - Beryllium
  - Cadmium
  - Chromium
  - Cobalt
  - Copper
  - Iron
  - Lead
  - Mercury
  - Manganese
  - Nickel
  - Selenium
  - Vanadium
  - Zinc

Volatile Organics
  - Nine Compounds

Non-Filterable Residue

Nitriloacetic Acid - Four Levels

Polychlorinated Biphenyls
  - Arochlor 1254
  - Arochlor 1016

Linear Alkalate Sulfonate

Additional information on quality control methods and the use of statistics in controlling analytical processes are found in many documents (EPA, 1979; EPA, 1976; Federal Register, 1978).

Data Reporting Procedures

The reporting of data occurs at several levels within and outside a given organization. The methods of reporting and the content of the report required for each level should be detailed in the quality assurance plan. The analysts or operators who collect and produce data may report to:

- Immediate supervisors
- Operations managers
- Quality assurance coordinator
- Regulatory agencies
- Regional or national data banks

The format and type of data reported should be geared to the needs of each level. In general, preprinted report forms should be used since they present the data in a consistent format and also serve as an instant reminder of the data necessary to satisfy the user's needs. Quality assurance for data reporting includes consistent, routine, and systematic checking of data at all levels to assure that the data being reported are the same as those obtained in the data-gathering activities. Among the steps required are:

- Checks of accuracy and precision of the data transcribing process where information is taken from strip charts or other continuous monitoring outputs.

- Systematic interaction among analysts and supervisors to assure that the data leaving the laboratory are the same data obtained from analysis of the samples.

- Duplication of portions of raw or partially processed data transmitted over telephone or other telemetry lines, as a check on the precision of transmission.

- Determination of the accuracy of transmission by checking the transmitted data against the data obtained by the sensor.

- Checks of data put onto computer files or into regional or national data banks for accuracy by retrieval and rechecking, preferably against the laboratory data. Data entered into a computer file such as STORET must be checked for accuracy each time a data set is entered. All data points must be rechecked, unless it is demonstrated that the accuracy attained warrants a reduction, but in no case should less than twenty percent of the data be rechecked.

In addition, results of the quality control tests or other statements concerning uncertainties in the results should be included to allow the data users to make valid judgments on the utility of the data. Routine quality control data are generally submitted to the appropriate state agency, or applicable permit granting authority. The frequency of reporting quality control data to state regulatory agencies will depend on the nature and requirements of the monitoring program. For ambient monitoring associated with energy conversion and production facilities, it is recommended that quality control data for ambient monitoring programs be reported to the appropriate state or permit granting agencies at least once every six months. Results of interlaboratory and collaborative quality control/assurance programs are to be reported to the agency coordinating the program.

Data Validation

Data validation is a quality control process in which data are screened and accepted or rejected based on a set of specific criteria. The criteria which may be used to judge whether data are to be accepted or rejected include:

- Special conditions unique to the measurement process.
- Specifications for calibration of tests and instruments.
- Results of statistical tests which can indicate whether or not the analysis was in control.
- Relationship of pollutants (e.g., high concentrations of sulfur dioxide and ozone cannot coexist, and simultaneous concentrations should be immediately suspect).
- Time-related variations expected for a given parameter.

The data validation process normally operates at the analyst-supervisor level, and includes routine examination of data for extreme values. Extreme values may be located by comparing current data to prior data obtained at a particular sampling site. The data used to locate extreme values may be the maximum and minimum concentrations for prior data from a given sampling site, and the criteria may also be specific for maximum and minimum concentrations for a given time period such as season, day or hour. Data which are from one to several orders of magnitude higher than the normal range of concentration are easily noted as possible spurious values. However, if a spurious value is only marginally higher or lower than the norm, spotting it could require specific knowledge of the environment from which that sample was taken. In either case, factors which could affect the concentration of that parameter should be checked. These may include:

- Sampling technique; was bottom sediment or floating scum picked up with the sample?
- Instrument operating conditions; was the proper amount of sample used, was the instrument in the proper operating mode?
- Calculations; were the proper factors used in calculation of concentration?
- Additional information, e.g., plant operating data may indicate that the plant's waste treatment system discharged high amounts of organic carbon during the time period in question.

If analytical errors are found, the data may be ruled invalid. If no analytical errors are found the data may still be ruled invalid if no specific cause of the spurious value can be found. The actions to be taken if data are ruled invalid may include:

- Rejection of data
- Repetition of measurement
- Use of data with special notation

Data collected during a time when accuracy, precision, or control chart data indicate that the analyses are out of control are often ruled invalid. The data may still be usable, providing that the variations applicable to the data can be determined. These data should be reported with a cautionary note describing the accuracy or precision of that set.

Whenever a suspicious value is noted, it should not be accepted or rejected without determining whether there is cause to do either. Each questionable value should be checked, and records maintained of such values; if values are shown to be invalid, the reasons for invalidation must be documented. Corrective action taken to prevent recurrence should also be noted. The records are, among other things, a useful source of information for judging the quality of future data.

The percentage of data which should be subjected to the validation process depends on the degree of reliability of the analytical equipment, and the percentage of past production of invalid data. As a general rule, ten percent of the data produced in the monitoring program should be subjected to the

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validation process. Some air pollution quality assurance documents recommend that a minimum of seven percent of the data be validated.

Calibration of Tests and Instruments

The methods to be used for calibration of the tests and instruments used in an ambient monitoring program should be thoroughly documented for each test or instrument used. They should list the specific standards and equipment required and the methods used to calibrate the tests. The methods should also provide specific instructions for obtaining and recording test data. The frequency and extent of calibration for tests and equipment required depends on several factors:

- Types of equipment or tests being used.
- Type of environment in which the tests are being performed.
- Manufacturers' recommendations.
- Level of accuracy required by the monitoring program.
- Applicable state or federal regulations.

The standards used to calibrate the tests and equipment must be documented as being traceable to standards provided by the National Bureau of Standards (NBS) or other primary standards. Measurements have traceability to designated standards only if rigorous evidence is produced on a continuing basis to show that the total measurement uncertainty relative to the specified standards is quantified (Belanger and Kieffer, 1979).

A specific protocol has been established for determining the true concentration of working standards for gaseous pollutants. It is to be used when calibrating an air pollution monitor with standards other than those supplied by the National Bureau of Standards (EPA, June 1978).

A certified primary standard obtainable from a commercial source shall be used for calibration when NBS standard reference materials are unavailable. The material used as a primary standard must have a known property that is stable and that can be accurately measured or derived from established chemical or physical constants (EPA, 1976). Transfer standards are materials used for routine calibration of field or laboratory equipment. These standards are calibrated against higher-level materials such as NBS standard reference materials or primary standards. Transfer standards used for calibration of tests and equipment shall be 4 to 10 times more accurate than the field or laboratory equipment being calibrated. For example, if a thermometer used to determine temperatures in the field must have an accuracy of ± 2°C, it must be calibrated against a thermometer with an accuracy of at least ± 0.5°C. Figure A-3 summarizes a coupled system of analytical methods and reference materials. The function of each component is to transfer traceability to the next higher level. This assures measurement compatibility in the system.

Table A-3 lists the standard reference materials available from the National Bureau of Standards. Many other reference materials and standards, such as for pesticides, are available from the EPA.

A detailed calibration plan must be in effect for each facility providing ambient monitoring data. The plan should include:

- Specified calibration intervals for each test and analytical instrument, and designations of satisfactory sources of calibration standards.
- A list of the required calibration standards for each test including the identification numbers for each standard.
- The mechanism used to establish traceability of the standards used to NBS standard reference materials or other primary standard.
- The operating conditions to be used during the calibration procedure for each test or instrument.
- A description of the calibration record system, including the data to be recorded and the manner in which records are to be maintained and distributed.

The intervals at which calibration of tests and equipment is performed can determine whether results from a monitoring program meet accuracy standards. In some cases, calibration intervals are specified by state and federal agencies; in the absence of regulations, a preliminary servicing schedule should be established, based on the operating time of the equipment. The establishment of calibration intervals is based upon required accuracy, degree of usage, and stability of the test or equipment. After evaluation of preliminary calibration results, the time period can be either lengthened or shortened as necessary, to provide positive assurance that the calibration interval is sufficient to maintain the accuracy of the system.

Preventive Maintenance

A preventive maintenance program increases or sustains the reliability of the measurement system. The schedule and activities associated with preventive maintenance must be clearly defined for each measurement system and its support

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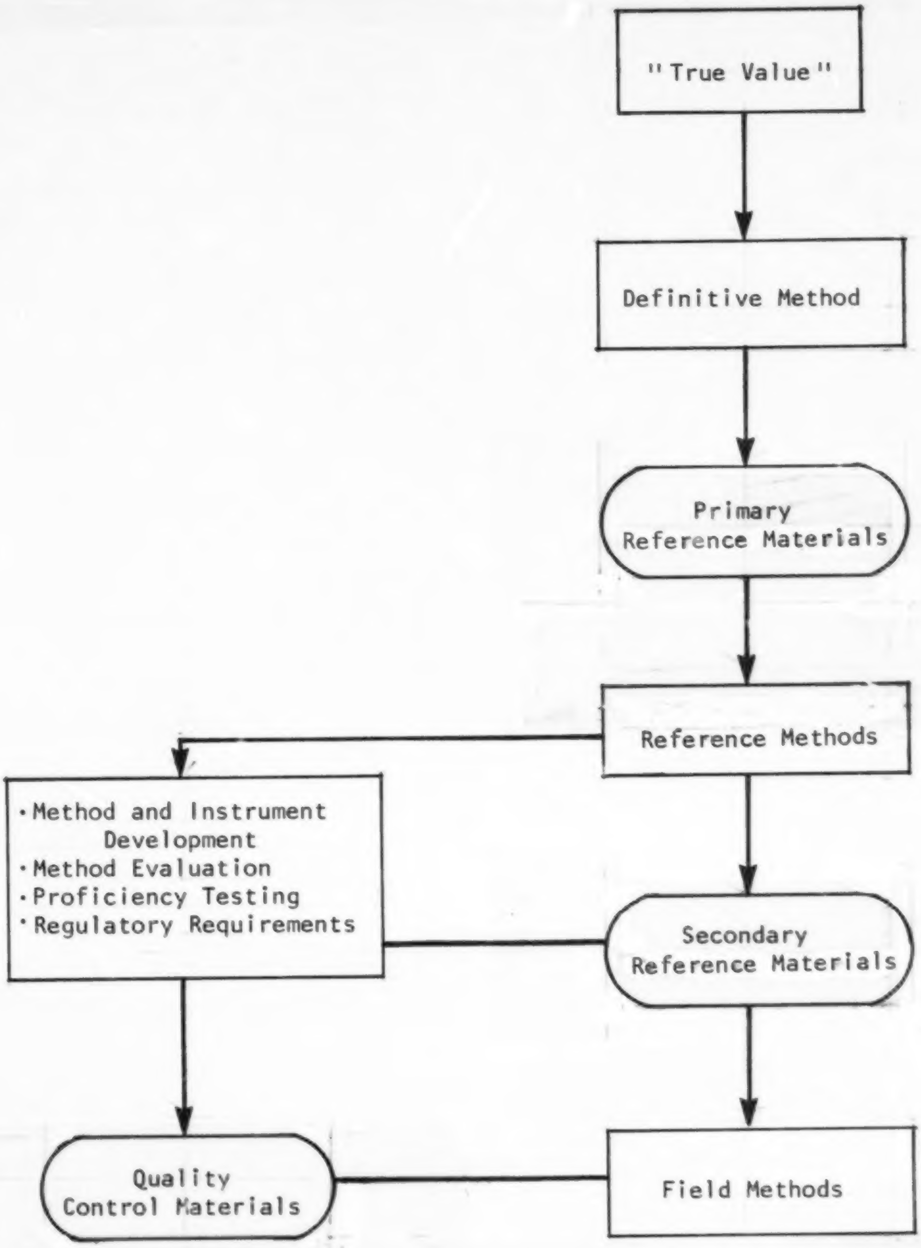
"True Value"
Definitive Method
Primary Reference Materials
Reference Methods
·Method and Instrument Development
·Method Evaluation
·Proficiency Testing
·Regulatory Requirements
Secondary Reference Materials
Quality Control Materials
Field Methods

Figure A-3. Idealized accuracy-based measurement network.

(Uriano, 1979)

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TABLE A-3. ENVIRONMENTAL STANDARD REFERENCE MATERIALS AVAILABLE FROM NATIONAL BUREAU OF STANDARDS
(National Bureau of Standards, 1978)

SRM No.	Type	Unit	Price ($)
	Analyzed Gases		
1609	Oxygen in N_2, 20.95 Mol. %	100 ml	120
1658	Methane in air, 0.95 ppm	cyl	283
1659	Methane in air, 9.5 ppm	cyl	283
1660	Methane (4 ppm) and Propane (1 ppm) in air	cyl	283
1661	Sulfur dioxide in N_2, 480 ppm	cyl	356
1662	Sulfur dioxide in N_2, 942 ppm	cyl	356
1663	Sulfur dioxide in N_2, 1497 ppm	cyl	356
1664	Sulfur dioxide in N_2, 2521 ppm	cyl	356
1665a	Propane in air, 2.8 ppm	cyl	282
1666a	Propane in air, 9.5 ppm	cyl	282
1667a	Propane in air, 48 ppm	cyl	282
1668a	Propane in air, 95 ppm	cyl	282
1669a	Propane in air, 475 ppm	cyl	282
1673a	Carbon dioxide in N_2, 0.95%	cyl	282
1674a	Carbon dioxide in N_2, 7.2%	cyl	282
1675a	Carbon dioxide in N_2, 14.2%	cyl	282
1677b	Carbon monoxide in N_2, 9.74 ppm	cyl	*
1678b	Carbon monoxide in N_2, 47.1 ppm	cyl	305
1679a	Carbon monoxide in N_2, 94.7 ppm	cyl	305
1680a	Carbon monoxide in N_2, 484 ppm	cyl	305
1681a	Carbon monoxide in N_2, 947 ppm	cyl	305
1683a	Nitric oxide in N_2, 50 ppm	cyl	*
1684a	Nitric oxide in N_2, 100 ppm	cyl	*

* To be renewed

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TABLE A-3 (Continued)

SRM No.	Type	Unit	Price ($)
1685a	Nitric oxide in N_2, 250 ppm	cyl	327
1686a	Nitric oxide in N_2, 500 ppm	cyl	327
1687a	Nitric oxide in N_2, 1000 ppm	cyl	327
2612	Carbon monoxide in air, 9.5 ppm	cyl	270
2613	Carbon monoxide in air, 18.0 ppm	cyl	270
2614	Carbon monoxide in air, 42.7 ppm	cyl	270
2619	Carbon dioxide in N_2, 0.5 mole %	cyl	353
2620	Carbon dioxide in N_2, 1.0 mole %	cyl	353
2621	Carbon dioxide in N_2, 1.5 mole %	cyl	353
2622	Carbon dioxide in N_2, 2.0 mole %	cyl	353
2623	Carbon dioxide in N_2, 2.5 mole %	cyl	353
2624	Carbon dioxide in N_2, 3.0 mole %	cyl	353
2625	Carbon dioxide in N_2, 3.5 mole %	cyl	353
2626	Carbon dioxide in N_2, 4.0 mole %	cyl	353
	Other Environmental SRM's		
1569	Brewers Yeast	50g	63
1570	Spinach, trace elements, botanical	60g	77
1571	Orchard leaves, trace element, botanical	75g	78
1573	Tomato leaves, trace elements, botanical	70g	77
1575	Pine needles, trace elements, botanical	70g	77
1577	Bovine liver	50g	98
1579	Powdered lead-base paint	35g	41
1621	Sulfur in residual fuel oil, 1.05 wt. %	100 ml	40
1623	Sulfur in residual fuel oil, 0.268 wt. %	100 ml	40
1624	Sulfur in distillate fuel oil, 0.211 wt. %	100 ml	40
1625	Sulfur dioxide permeation tube, 10 cm	ea	85
1626	Sulfur dioxide permeation tube, 5 cm	ea	85
1627	Sulfur dioxide permeation tube, 2 cm	ea	85
1629	Nitrogen dioxide permeation device	ea	88
1630	Trace mercury in coal	50g	53
1632	Trace elements in coal	75g	77

(Continued)

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TABLE A-3 (Continued)

SRM No.	Type	Unit	Price ($)
1633	Trace elements in coal fly ash	75g	77
1634	Trace elements in fuel oil	100 ml	77
1636	Lead in reference fuel, four concentrations	set (12)	61
1637	Lead in reference fuel, three concentrations	set (12)	61
1638	Lead in reference fuel, one concentration	set (12)	61
1641	Mercury in water, 1.49 ug/ml	120 ml	62
2661	Benzene on charcoal	set (8)	87
2662	m-Xylene on charcoal	set (8)	87
2663	p-Dioxane on charcoal	set (8)	87
2664	1, 2-Dichloroethane on Charcoal	set (8)	87
2665	Chloroform on charcoal	set (8)	87
2666	Trichloroethylene on Charcoal	set (8)	87
2667	Carbon Tetrachlorine on Charcoal	set (8)	87
2671	Freeze-dried urine certified for fluorine	set (2)	82
2672	Freeze-dried urine certified for mercury	set (2)	82
2675	Beryllium on filter media	set (3)	82
2676	Metals on filter media	set (2)	*

* To be renewed

equipment. The criteria for determining the need for preventive maintenance, and the schedule on which maintenance should be performed include:

- Type of environment in which the equipment is being used.
- Manufacturers' recommendations as found in the instruction manuals for each instrument or equipment.
- Specific mandates listed in the official or reference method applicable to the measurement of a given parameter.
- Operational history of the specific instrument or equipment.

Preventive maintenance steps, their frequency, and the derived data should be documented. A record of all routine and nonroutine servicing of equipment shall be maintained. The preventive maintenance and other maintenance records should be used to:

- Revise maintenance schedules to maximize time of operation for each instrument.
- Maximize quality of data output.
- Minimize loss of data due to equipment failure.
- Guide to development of an adequate parts inventory and schedule of replacement.

Equipment that is used on a continuous basis, such as air pollution monitors and automatic water monitors and sampling equipment, commonly requires daily service or performance checks. The amount of servicing is dictated by the nature of the equipment, the environmental conditions that can be maintained for the monitor, and the degree of accuracy required of the monitor. Equipment used in the laboratory under controlled environmental conditions may require only periodic servicing. Service and performance checks, however, should be routine steps in each analytical procedure. It is recommended that, where available, service contracts from the manufacturers be obtained for at least the major analytical equipment. This will assure that the functional capabilities of the equipment are maintained.

SUMMARY

A quality assurance program is a system of activities for integrating the quality planning, quality assessment and quality improvement efforts of an organization. The objectives of a quality assurance program are to:

- Minimize systematic and random variability in the measurement and data collection process.

- Provide for prompt detection and correction of conditions which would contribute to the production of poor quality data.
- Collect and supply information necessary to describe the quality of the data.
- Evaluate the overall adequacy of the data-gathering process insofar as it affects data quality.

Elements of a quality assurance program fall into two general groups: organization, and documentation of operations and procedures. The elements within the organization group are the administrative activities necessary to manage the program, provide the necessary facilities, train the personnel, and audit the adequacy of the program. The elements of the second group are the operational activities required for a monitoring program, such as sample site selection, sampling, analysis, preventive maintenance and data reporting.

A primary management responsibility is to designate a person to administer the quality assurance activities of the organization and coordinate these activities with appropriate regulatory agencies. The quality assurance coordinator works with both management and supervisory personnel to develop and implement training programs, determine propriety of methods, select equipment, develop facilities, and determine how the quality of monitoring data should be measured.

The quality assurance plan should document the development and implementation responsibilities of each worker. Documentation of the operational procedures of an ambient monitoring program are required to assure that:

- The sampling network design and sampling techniques provide representative samples of the ambient medium.
- Sample handling and storage maintain the integrity and representativeness of samples and meet custody requirements.
- The analytical methods are applicable and any modifications are properly justified.
- External and internal quality control checks are performed, and accuracy and precision can be demonstrated to be within acceptable limits.
- Data are reported in a format appropriate for each user.

- Calibration of tests and instruments are performed at regular intervals and the criteria for calibration are known.
- Preventive maintenance schedules are known and followed and documentation of acceptability of instruments is available.

Documentation of these quality assurance activities is required to: (1) unify the various elements and personnel involved in the program, (2) outline the responsibilities and time frame for performing the various tasks, (3) describe the action required to eliminate any identified deficiencies, (4) ensure that valid data are being generated by the monitoring program and that this validity can be adequately demonstrated at a later date.

REFERENCES

Buchanan, J. 1976. Guidelines for Demonstration Project Quality Assurance Programs. Industrial Environmental Research Laboratory, U.S. Environmental Protection Agency. Research Triangle Park, North Carolina.

Dalton•Dalton•Newport. 1978. Guidelines for Multimedia Environmental Monitoring of DOE Fossil Energy R&D Facilities, FE-2495-6A01. Dalton•Dalton•Newport, Cleveland, Ohio.

Davis and DeWiest. 1966. Hydrogeology. New York: John Wiley and Sons.

Environmental Science and Technology. 1978. QA Report: Federal Environmental Monitoring - Will the Bubble Burst? Environmental Science and Technology, 12(12):1264-1269.

Federal Register.

December 1 1976	Guidelines Establishing Test Procedures for the Analysis of Pollutants.
August 7 1978	Part II: Air Quality Surveillance and Data Reporting, Proposed Regulatory Revisions.

Murthy, K.S., and D.B. Henschel. 1978. Environmental Assessment of Fluidized Bed Combustion: Status and Results. Presented at Environmental Assessment of Solid Fossil Fuel Symposium, 71st Annual AI CheE Meeting, Miami Beach, Fla., November 1978.

National Bureau of Standards. 1978. Catalog of NBS Standard Reference Materials. NBS Special Publication 260. National Bureau of Standards, Washington, D.C.

Smith, F., and D.E. Wagoner. 1974. Guidelines for Development of a Quality Assurance Program. Vol. IV: Determination of Particulate Emission from Stationary Sources. National Environmental Research Center, U.S. EPA Research Triangle Park, North Carolina.

Todd, D. 1967. Groundwater Hydrology. New York: John Wiley and Sons, Inc.

U.S. Environmental Protection Agency.

1976 Quality Assurance Handbook for Air Pollution Measurement Systems, Vol. I Principles. Office of Research and Development. U.S. EPA, Research Triangle Park, North Carolina.

May 1978a Ambient Monitoring Guidelines for Prevention of Significant Deterioration. Office of Air Quality Planning and Standards, U.S. EPA Research Triangle Park, North Carolina.

May 1978b NEIC Policies and Procedures Manual, National Enforcement Investigation Center, U.S. EPA Denver, Colorado.

June 1978 Traceability Protocol for Establishing True Concentrations of Gases for Calibration and Audits of Air Pollution Analyzers (Protocol No. 2) Environmental Monitoring and Support Laboratory, U.S. EPA Research Triangle Park, North Carolina.

1979 Handbook for Analytical Quality Control in Water and Wastewater Laboratories. Methods Development and Quality Assurance Laboratory, U.S. EPA. Cincinnati, Ohio.

Uriano, G.A. 1979. The Use of Standard Reference Materials For Quality Assurance of Environmental Measurements. Proceedings of the National Conference on Quality Assurance of Environmental Measurements, Denver, Colorado, November 1978.

Walton, W.C. 1970. Groundwater Resources Evaluation. New York: McGraw Hill, Inc.

BIBLIOGRAPHY

OFFICIAL METHODS AND SOURCES OF METHODS FOR SAMPLE COLLECTION, ANALYSIS AND QUALITY ASSURANCE

Annual Book of ASTM Standards. (Part 31) Water. 1975. American Society for Testing and Materials, Philadelphia, Pennsylvania.

Biological Field and Laboratory Methods for Measuring the Quality of Surface Waters and Effluents. 1973. Office of Research and Development. U.S. Environmental Protection Agency, Cincinnati, Ohio

Manual of Methods for Chemical Analysis of Water and Wastes. 1979. Office of Technology Transfer, U.S. Environmental Protection Agency, Washington, D.C.

Methods of Air Sampling and Analysis. 1977. 2nd Edition. American Public Health Association, Washington, D.C.

NIOSH Manual of Analytical Methods. 1977. 2nd Edition, Vol. 1-3. National Institute of Occupational Safety and Health, U.S. DHEW, Cincinnati, Ohio.

Quality Assurance Handbook for Air Pollution Measurement Systems. 1977. Vol. II: Ambient Air Specific Methods. Environmental Monitoring and Support Laboratory, U.S. EPA Research Triangle Park, North Carolina.

Standard Methods for the Examination of Water and Wastewater. 1975. 14th Edition. American Public Health Association, Washington, D.C.

In addition to the primary sources of analytical methods, there are numerous other sources of information usable in establishing and operating an ambient environmental monitoring program. These sources contain information on site selection analysis, sample collection, statistics and quality assurance. They include:

ASTM Standards on Precision and Accuracy for Various Applications. 1977. American Society for Testing and Materials, Philadelphia, Pennsylvania.

Ambient Monitoring Guidelines for Prevention of Significant Deterioration. 1978. Office of Air Quality Planning and Standards, U.S. EPA Research Triangle Park, North Carolina.

Brown, E.M., and M.W. Skougstad. 1970. Methods for Collection and Analysis of Water Samples for Dissolved Minerals and Gases. U.S. Geological Survey Techniques, Water Resources Inc. Book 5.

Buchanan, J., and F. Smith, 1976. Guidelines for Development of a Quality Assurance Program. Vol. XVI - Method for the Determination of Nitrogen Dioxide in the Atmosphere. Environmental Monitoring and Support Laboratory, U.S. EPA, Research Triangle Park, North Carolina.

Duncan, A.J. 1965. Quality Control and Industrial Statistics. 3rd Edition. Homewood, Illinois: Richard D. Irwin Inc.

Grubles, F.E. 1969. Procedures for Detecting Outlying Observations in Samples. Technometrics, II-1:1-21.

Guidelines for Siting and Exposure of Meteorological Instruments for Environmental Purposes. 1976. Meteorological and Assessment Division, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.

Hamilton, C.E., (Ed). 1978. Manual on Water. American Society for Testing and Matials, STP 442A, Philadelphia, Pennsylvania.

Handbook for Analytical Quality Control in Water and Wastewater Laboratories. 1979. Technology Transfer, U.S. Environmental Protection Agency, Washington, D.C.

Handbook for Monitoring Industrial Wastewater. 1973. Technology Transfer, U.S. Environmental Protection Agency, Washington, D.C.

Kolnsberg, H.J. 1976. Technical Manual for Measurement of Fugitive Emissions, Upwind/Downwind Sampling Method for Industrial Emission. Office of Research and Development. U.S. Environmental Protection Agency, Washington, D.C.

Mandel, John. 1964. The Statistical Analysis of Data. New York: Interscience Publishers.

Minimal Requirements for a Water Quality Assurance Program. 1975. Environmental Monitoring and Support

Laboratory, U.S. Environmental Protection Agency, Cincinnati, Ohio.

Quality Assurance Handbook for Air Pollution Measurement Systems. 1976. Vol. 1, Principles. Environmental Monitoring and Support Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.

Rainwater, F.H., and L.L. Thatcher. 1960. Methods of Collection and Analysis of Water Samples. U.S. Geological Survey, Water Supply Paper No. 1454.

Smith, F., and A.C. Nelson, Jr. 1973. Guidelines for Development of a Quality Assurance Program. Reference Method for Continuous Measurement of Carbon Monoxide in the Atmosphere. Office of Research and Monitoring Quality Assurance, U.S. EPA, Research Triangle Park, North Carolina.

Smith, F., and A.C. Nelson, Jr. 1973. Guidelines for Development of a Quality Assurance Program: Reference Method for Determination of Suspended Particulates in the Atmosphere (High Volume Method). Quality Assurance and Environmental Monitoring Laboratory, U.S. EPA, Research Triangle Park, North Carolina.

Smith, F., and A.C. Nelson, Jr. 1973. Guidelines for Development of a Quality Assurance Program: Reference Method for the Determination of Sulfur Dioxide in the Atmosphere. Quality Assurance and Environmental Monitoring Laboratory, U.S. EPA, Research Triangle Park, North Carolina.

Wastewater Sampling Methodologies and Techniques. 1974. Office of Technology Transfer, U.S. Environmental Protection Agency, Washington, D.C.

Water Pollution Assessment. 1974. Automatic sampling and Measurement. American Society for Testing and Materials, STP582, Philadelphia, Pennsylvania.

Wood, W.W. Guidelines for Collection and Field Analysis of Groundwater Samples for Selected Unstable Constituents. U.S. Geological Survey Techniques, Water Resources Inv.

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APPENDIX B

LIST OF LAWS, REGULATIONS, AND EXECUTIVE ORDERS PERTAINING TO ENVIRONMENT AND SAFETY AND HEALTH REQUIREMENTS

LAWS

Environment

- Cultural Resources Protection
  - Historic Sites Act of 1935
  - National Historic Preservation Act of 1966, As Amended
  - Archaeological and Historic Preservation Act of 1974
  - Archaeological Resources Protection Act of 1979
- Water Quality and Water Resources
  - Safe Drinking Water Act of 1974
  - Federal Water Pollution Control Act of 1972, As Amended
  - Federal Water Project Recreation Act of 1965, As Amended
  - Water Resources Research Program Act of 1964
  - Rivers and Harbors Act of 1899
  - Wild and Scenic Rivers Act of 1968
  - Water Resources Planning Act of 1965
  - Soil and Water Resources Conservation Act of 1977
- Floodplains, Wetlands, and Coastal Zones
  - Coastal Zone Management Act of 1972, As Amended
  - Estuary Protection Act of 1968
  - National Flood Insurance Act of 1968, As Amended
- Wildlife
  - Endangered Species Act of 1973, As Amended
  - Fish and Wildlife Coordination Act of 1934, As Amended
  - Fish and Wildlife Conservation at Small Watershed Projects
- Public Land, Open Space, and Recreation
  - National Trails System Act of 1968, As Amended
  - Wilderness Act of 1964
  - National Forest Management Act of 1976
  - Mineral Leasing Act Amendments of 1973
  - Land and Water Conservation Act of 1965, As Amended
  - Forest and Rangeland Renewable Resources Planning Act of 1974, As Amended

  - Oceanography and Marine Environment
    - Deepwater Port Act of 1974
    - Marine Protection, Research and Sanctuaries Act of 1972, As Amended
    - Marine Mammal Protection Act of 1972, As Amended
    - Fishery Conservation and Management Act of 1976
  - Air Quality and Noise
    - Clean Air Act of 1963, As Amended
    - National Emission Standards Act of 1967
    - Noise Pollution and Abatement Act of 1970
    - Noise Control Act of 1972
  - Energy
    - Energy Supply and Environmental Coordination Act of 1974
    - Trans-Alaska Pipeline Act of 1973
    - Federal Non-Nuclear Energy Research and Development Act of 1974
    - Energy Policy and Conservation Act of 1975
    - Surface Mining Control and Reclamation Act of 1977
    - Federal Power Act of 1935, As Amended
    - The Outer Continental Shelf Lands Act of 1953, As Amended
    - Alaska Natural Gas Transportation Act of 1976
    - The Atomic Energy Act of 1954, As Amended
    - The Natural Gas Act of 1938, As Amended
  - Hazardous and Solid Wastes
    - Resources Conservation and Recovery Act of 1976
  - Other Environmental Laws
    - National Environmental Policy Act of 1969
    - Demonstration Cities and Metropolitan Development Act of 1966

- Safety and Health
  - Occupational Safety and Health Act of 1970
  - Toxic Substances Control Act of 1976
  - Ports and Waterways Safety Act of 1972
  - Federal Coal Mine Health and Safety Act of 1969, As Amended
  - Hazardous Materials Transportation Act
- Property
  - Federal Land Policy and Management Act of 1976
  - Antiquities Act of 1906

REGULATIONS

- Environment
  - Council on Environmental Quality's Regulations for the Implementation of the National Environmental Policy Act
  - Advisory Council on Historic Preservation; Procedures for Historic Preservation

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EXECUTIVE ORDERS

Environment

- 11514, Protection and Enhancement of Environmental Quality
- 11523, Establishing the National Industrial Pollution Control Council
- 11574, Administration of the Refuse Act Permit Program
- 11738, Providing for Administration of the Clean Air Act and the Federal Water Pollution Control Act with Respect to Federal Contracts, Grants, or Loans
- 11742, Delegating to the Secretary of State Certain Functions Under the Federal Water Pollution Control Act with Respect to Negotiations of International Agreements
- 11747, Delegating Authority of the President Under the Water Resources Planning Act
- 11987, Exotic Organisms
- 11988, Floodplain Management
- 11990, Protection of Wetlands
- 12113, Providing for Independent Water Project Review
- 12114, Environmental Effects Abroad of Major Federal Actions
- 12129, Critical Energy Facility Program

Safety and Health

- 11807, Occupational Safety and Health Programs For Federal Employees

Property

- 11593, Protection and Enhancement of the Cultural Environment
- 11643, Environmental Safeguards on Activities for Animal Damage Control in Federal Lands
- 11989, Off-Road Vehicles on Public Lands
- 12088, Federal Compliance with Pollution Control Standards

OTHER RELEVANT EXECUTIVE ORDERS AND GUIDANCE

- 11490, Assigning Emergency Preparedness Functions to Federal Departments and Agencies
- 12044, Improving Government Regulations

OTHER GUIDANCE DOCUMENTS

Environment

- Water Resources Council, Guidance for Floodplain Management
- Water Resources Council, Principles and Standards
- Council on Environmental Quality Memorandum on Prime and Unique Farmlands
- OMB Circular A-95-Early Coordination
- OMB Circular A-109-Major System Acquisition

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